Process modeling of very-high-gravity fermentation system under redox potential-controlled conditions

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By

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Key words: Very-high-gravity fermentation, Redox potential control, Process simulation, Superpro, Aspen Plus, Icarus, Economic evaluation, CO_2 storage

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ABSTRACT

The objective of this study is to evaluate and compare, both technically and economically, various glucose feeding concentrations and different redox potential settings on ethanol production under very-high-gravity (VHG) conditions. Laboratory data were collected for process modeling and two process models were created by two individual process simulators. The first one is a simplified model created and evaluated by Superpro Designer. The second one is an accurate model created by Aspen Plus and evaluated by Aspen Icarus Process Evaluator (Aspen IPE). The simulation results of the two models were also compared.

Results showed that glucose feeding concentration at 250±3.95 g/L to the fermentor resulted in the lowest unit production cost (1.479 $/kg ethanol in the Superpro model, 0.764 $/kg ethanol in the Aspen Plus model), with redox potential control effects accounted. Controlling redox potential at -150 mV increased the ethanol yield under VHG fermentation conditions while no significant influences were observed when glucose feeding concentration was less than 250 g/L. Results of product sales analysis indicated that for an ethanol plant with a production rate of 85~130 million kg ethanol/year, only maintaining the glucose feeding concentration to the fermentor at around 250 g/L resulted in the shortest payout period of 5.33 years in average,, with or without redox potential control. If 300±6.42 g/L glucose feeding concentration to the fermentor is applied, it is essential to have the redox potential only controlled at -150 mV in the fermentor to limit the process payout period within 6 years. In addition, fermentation processes with glucose feeding concentration at around 200 g/L to the fermentor were estimated to be unprofitable under all studied conditions.

For environmental concerns, two disposal alternatives were presented for CO_2 produced during fermentation process rather than emission into atmosphere. One is to sell CO_2 as byproduct, which brought 1.52 million $/year income for an ethanol plant with a capacity of 100 million kg ethanol/year. Another option is to capture and transport CO_2 to deep injection sites for geological underground storage, which is already a safe and mature technology in North America, and also applicable to many other sites around the world. This would roughly add 4.78 million dollars processing cost annually in the studied scenario. Deep injection of captured CO_2 from ethanol plants prevents emission of CO_2 into the atmosphere, thus makes it environmental friendly.

Key words

Very-high-gravity fermentation, Redox potential control, Process simulation, Superpro, Aspen Plus, Icarus, Economic evaluation, CO_2 storage

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NOMENCLATURE

Symbol	Definition	Units
ASME	American Society of Mechanical Engineering	
CF	Conversion Factor	
CS	Carbon Steel	
DDGS	Dried Distillers Grains with Solubles	
ID	Inner Diameter	ft or m
MW	Molecular Weight	g/gmol
NPV	Net Present Value	
P and I	Piping and Instrumentation	
PC	Purchasing Cost	US $
SS304	Stainless Steel 304	
SS316	Stainless Steel 316	
VVM	Volume per Volume per Minute	
YDM	Yeast Dry Matter	

CHAPTER 1 INTRODUCTION

1.1 Background

The use of ethanol as an alternative transportation fuel provides tremendous environmental and economic advantages and it enables countries to achieve energy security and independence (Duncan, 2003). The recent increases in petroleum prices and government legislation and regulations have stimulated the production of fuel ethanol. The demand of ethanol for producing reformulated gasoline and for use as an extender of the gasoline supplies is expected to accelerate the growth rate of the ethanol industry as long as petroleum prices remain high (Eidman, 2006).

Currently, the most significant barrier to wider use of fuel ethanol is its cost. However, fuel ethanol has the potential to be cost-competitive with petroleum fuels if there are government incentives and continued progress with both conventional and advanced ethanol production technologies (Zhang *et al.*, 2003).

In fact, in the past decade, the conventional fermentation process has been improved through the application of very high gravity (VHG) technology capable of fermenting higher-density mashes with a higher initial sugar level (Thomas *et al.*, 1993). This exciting technology aims at increasing both the rate of fermentation and the final ethanol concentration and thereby reducing processing costs (Ingledew, 1993).

Nevertheless, the economic advantages of VHG technology are accompanied by a number of problems: as the sugar concentration increases, the yeast is exposed to severe conditions, such as the increase of both osmotic pressure and produced ethanol, nutrient deficiencies, especially dissolved oxygen and assimilable nitrogen. These may result in a significant delay in fermentation and drop in yeast viability (Pratt *et al.*, 2003; Casey *et al.*, 1984; Day *et al.*, 1975; White, 1978).

In today's fuel market, every penny in cost savings makes a difference. Thus, a deeper understanding of stress-tolerance mechanisms of *Saccharomyces cerevisiae*, which may lead to new process design that may improve yield and performance in the conversion process are essential to making fuel ethanol competitive with gasoline.

1.2 Objectives

As mentioned above, the objective of this study is mainly to evaluate and compare, both technically and economically, various glucose feeding concentrations and different redox potential settings on ethanol production under very-high-gravity (VHG) conditions, rather than estimating accurate economic evaluation results for large scale production.

To achieve this, a model simplified and modified from Kwiatkowski *et al.* (2006) for the process of VHG fermentation was firstly established using Superpro Designer v7.0 (Intelligen, INC. 2326 Morse Avenue, Scotch Plains, NJ07076, USA). Parameters of the fermentation process, such as glucose and ethanol concentrations, yeast cell viability, dry weight of biomass, redox potential settings, was determined based on experimental data collected in laboratory experiments by Lin *et al.* (2010).

After completion of the model, data collected in laboratory experiments were applied to the model for process simulation and economical evaluation, results of the evaluation were analyzed. Since the software Superpro Designer used in the first model has a disadvantage that the number of unit procedures is limited to be less than 25 in one process model, therefore the liquefaction and saccharification sections as well as downstream treatment of DDGS stream of an ethanol producing process were purposely ignored, hence the first model is still not accurately reflecting the conditions in a real ethanol plant. In addition, because of the number limitation of unit procedures used in the Superpro model, recycle streams that used in the whole ethanol producing process scale to save energy were also not applicable, which may have certain influence on economical evaluation.

To overcome the disadvantage of the fist model, Aspen Plus 2006 was introduced to create a more accurate model of an ethanol plant, and Aspen Icarus Process Evaluator 2006 (Aspen IPE) was used for economical evaluation, to give better understandings of how various glucose feeding concentrations and different redox potential settings affect ethanol production under very-high-gravity (VHG) conditions.

1.3 Thesis organization

Chapter 1 is the introduction to this thesis, with a summary of project background, objectives, and the organization of this thesis.

Chapter 2 is a literature review of the field of fuel ethanol and process modeling of ethanol production, as well as the knowledge gap of process modeling for VHG fermentation.

Chapter 3 covers the methods to collect experimental data, descriptions of software used in process modeling. Detailed descriptions of modeled processes were also presented with general process and design data.

Chapter 4 provides the results of evaluation of the two models, along with discussions of findings.

Chapter 5 states conclusions of the work results and suggests possible directions for future work.

CHAPTER 2 LITERATURE REVIEW

2.1 Fuel ethanol production

Ethanol is widely used as fuel, solvent, disinfectant, medicine and feedstock for the synthesis of other chemical products. In addition, ethanol has high octane number and high latent heat of vaporization, thus it can also be blended with gasoline to use as transportation fuel. More importantly, since the future energy supply must meet with a substantial reduction of greenhouse gas emissions (Ko *et al*., 2010), bio-ethanol has also environmental advantages in comparison with fossil fuels.

As a relatively low-cost alternative fuel other than gasoline, there are several environmental benefits by using ethanol or an ethanol blend gasoline in place of unblended gasoline. First of all, ethanol is considered to be better for the environment than gasoline. Ethanol-fueled vehicles produce lower carbon monoxide and carbon dioxide emissions, and the same or lower levels of hydrocarbon and oxides of nitrogen emissions. E85, a blend of 85 percent ethanol and 15 percent gasoline, also has fewer volatile components than gasoline, which means fewer emissions from evaporation. Adding ethanol to gasoline in lower percentages, such as 10 percent ethanol and 90 percent gasoline (E10), reduces carbon monoxide emissions from the gasoline and improves fuel octane.

Also, ethanol is broadly available and easy to use. Flexible fuel vehicles that can use E85 are widely available and come in many different styles from most major auto manufacturers. E85 is also widely available at a growing number of stations throughout the United States. Flexible fuel vehicles have the advantage of being able to use E85, gasoline, or a combination of the two, giving drivers the flexibility to choose the fuel that is most readily available and best suited to their needs.

Agricultural crops such as corn, wheat are commonly used as the raw material for bio-ethanol production. Since the rising requirement of using non-food feedstocks for fermentation, starch based feedstock like winter barley (Gibreel *et al.*, 2008; Nghiem *et al*., 2010), and non-starch based feedstocks such as cellulose and lignocellulose rich feedstocks (Nevoigt, 2008), are also introduced in industrial fuel ethanol production.

Regardless of what feedstocks are used, they all have to be converted to fermentable sugars before fermentation, otherwise the yeast cells can not utilize them. For starch based feedstocks, α-amylase is used for the conversion process which contains liquefaction and saccharification. And for non-starch based feedstocks, dilute acid process and concentrated acid process are applied by using sulfuric acid and hydrochloric acid for the hydrolization process to obtain fermentable sugars (Wingren *et al.*, 2003).

The two dominating processes that use enzymes for saccharification are separate hydrolysis and fermentation (SHF) and simultaneous saccharification and fermentation (SSF) (Wingren *et al.*, 2003). SSF has been regarded as the major option because for various substrates and under varying pretreatment conditions it results higher yields and shorter residence times according to Wingren *et al.*.

The alcoholic fermentation is mainly a conversion process of glucose to ethanol using active dry yeast (*Saccharomyces cerevisiae*). In the past decades, ethanol-tolerant strains of *S. cerevisiae* have become available for industrial fermentation, allowing fermentation under very high concentrations of carbohydrates. Usually, sugar concentrations in excess of 200 g/L are not used under industrial conditions because increasing concentrations of ethanol retard the growth of yeasts and fermentation eventually arrests (Thomas and Ingledew, 1990). However, the industrial yeast strains used in bio-ethanol fermentation can grow in fermentation broth with 300 g/L initial glucose but slow fermentation rate (Zhao and Lin, 2003). Generally, VHG fermentation means bio-ethanol fermentation with glucose feeding concentration greater than 250 g/L.

According to EthanolIndia (http://www.ethanolindia.net/molecular_sieves.html, August 1, 2011), distillation columns are used to separate ethanol from the primary product stream of the fermentor. Pure ethanol is an important product required by industry. Ethanol as manufactured is rectified spirit, which is 94.68% (v/v) ethanol, and rest is water. It is not possible to remove remaining water from rectified spirit by straight distillation as ethanol forms a constant boiling mixture with water at this concentration and is known as azeotrope. Therefore, special process for removal of the remaining water is required for manufacture of absolute pure ethanol.

In order to extract water from ethanol it is necessary to use some dehydrate, which is capable of separating water from ethanol. Simple dehydrate is unslaked lime, also known as quick lime. Industrial ethanol is taken in a reactor and quick lime is added to it and the mixture is left over night for complete reaction. It is then distilled in fractionating column to get absolute ethanol. Water is retained by quick lime. This process is used for small-scale production of absolute ethanol by batch process.

Most of the ethanol dehydration plants for production of pure ethanol are based on azeotropic distillation. It is a mature and reliable technology capable of producing a very dry product. From feed tank, rectified spirit is pumped to the stripper/rectifier column. A partial steam of vapors from the column are condensed in condenser and sent back to the column as reflux. Rest of the vapors are passed through a super-heater and taken to the molecular sieve units for dehydration. The vapor passes through a bed of molecular sieve beads and water in the incoming vapor stream is adsorbed on the molecular sieve material and anhydrous ethanol vapor exists from the molecular sieve units. Hot anhydrous ethanol vapor from the molecular sieve units is condensed in the molecular sieve condenser. The anhydrous ethanol product is then further cooled down in the product cooler, to bring it close to the ambient temperature.

The two molecular sieve units operate sequentially and are cycled so that one is under regeneration while the other is under operation, adsorbing water from the vapor stream. The regeneration is accomplished by applying vacuum to the bed undergoing regeneration. The adsorbed water from the molecular sieves material desorbs and evaporates into the ethanol vapor stream. This mixture of ethanol and water is condensed and cooled against cooling tower water in the molecular sieve regenerant condenser. Any uncondensed vapor and entrained liquid leaving the molecular sieve regenerant condenser enters the molecular sieve regenerant drum, where it is contacted with cooled regenerant liquid.

The cooled regenerant liquid is low in ethanol concentration, as it contains all the water desorbed from the molecular sieve beds. This low ethanol liquid is recycled back to the stripper column for recovering the ethanol. The water leaves from the bottom of the column and contains only traces of ethanol.

The molecular sieve separation system is an advanced control system, developed through years of experience, to provide sustained, stable, automatic operation, and at the mean time requires only minimal labor and achieves near theoretical recovery of ethanol.

2.2 Process modeling of fermentation system

There is an increasing trend that bio-ethanol fermentation is handled by a process simulator in the recent years (Ko *et al*., 2010; Kwiatkowski *et al.*, 2006; Ramirez *et al.*, 2009; Taylor *et al.*, 2000; Wingren *et al.*, 2003). The whole fermentation process can be simulated in a process flow diagram (PFD) by computers, with input data and process parameters obtained from real plants or manufacturers, to perform material and mass balance calculations as well as financial analysis including capital and operating costs, revenues, earnings, and return on investment in a relatively short time scale using certain simulators. The advantage of using process models to simulate a real process is to save time and labor in design before construction, and to obtain data for capital investment decisions. Furthermore, many relevant process parameters can be easily adjusted for certain scenarios to make it possible to simulate the industrial process in conjunction with lab data, and to understand how little variations in input would be reflected in the output results.

Process simulations have been reported for a whole bio-ethanol fermentation process from raw material such as corn to ethanol (Kwiatkowski *et al.*, 2006; Taylor *et al.*, 2000), or simply the corn milling, liquefaction and saccharification process (Ochoa *et al.*, 2007; Rajagopalan *et al.*, 2005; Ramirez *et al.*, 2009; Sainz *et al.*, 2003). Some of these studies were reviewed in the following.

2.2.1 Superpro Designer

SuperPro Designer is a professional process simulator developed by Intelligen Incorporated (2326 Morse Avenue, Scotch Plains, NJ07076, USA), which facilitates modeling, evaluation and optimization of integrated processes in a wide range of industries (Pharmaceutical, Biotech, Specialty Chemical, Food, Consumer Goods, Mineral Processing, Microelectronics, Water Purification, Wastewater Treatment, Air Pollution Control, etc.).

Besides process modeling, Superpro Designer has many advanced convenient features such as material and energy balances calculations, extensive databases for chemical component and mixture as well as equipment and resource, equipment sizing and costing, thorough process economics, Waste stream characterization, etc. All these features are quite useful when analyzing the process models.

In Kwiatkowski *et al.*'s (2006) study, the simulation software Superpro Designer Version 5.5 Build 18 (Intelligen Inc., Scotch Plains, NJ), a lower enterprise version rather the higher academic version used in my own study, was used to develop a corn dry-grind process model for an ethanol plant with 119 million kg ethanol/year capacity. And the model is based on data gathered from ethanol producers, technology suppliers, equipment manufacturers, and engineers working in the industry. Intended applications of this model include: evaluating existing and new grain conversion technologies, determining the impact of alternate feedstocks, and sensitivity analysis of key economic factors.

Shelled corn is assumed to be the primary feedstock of this model, and its cost has the greatest impact on the cost of producing ethanol. With the data used in Kwiatkowski's model, the unit production cost of ethanol is approximately 0.342 $/kg. Also, starch content variation in the feed, as a result of starch content variation in corn, causes variations in Production rate, for example, a reduction from 119 to 110 million kg ethanol/year as the amount of starch in the feed was lowered from 59.5% to 55% (w/w).

2.2.2 Aspen Plus and Aspen Icarus Process Evaluator

Aspen Plus is another very powerful process modeling tool developed by Aspen Technology Incorporated (200 Wheeler Road, Burlington, Massachusetts 01803, USA) for conceptual design, optimization, and performance monitoring for the chemical, polymer, specialty chemical, metals and minerals, and coal power industries. Aspen Plus is a core element of AspenTech's (Aspen Technology Inc.) aspenONE® Process Engineering applications. Aspen Plus has many advanced practical features such as best-in-class physical properties methods and data, improved conceptual design workflow, scalability for large and complex processes, etc.

As a powerful process simulator, after the completion of process modeling and calculations of mass and energy balances, the simulation results can be generated and sent to another Aspen utility, Aspen Icarus Process Evaluator or Aspen IPE, which is specialized for further economical evaluations.

AspenTech's Icarus Process Evaluator (IPE) is designed to automate the preparation of detailed designs, estimates, investment analysis and schedules from minimum scope definition, whether from process simulation results or sized equipment lists. It allows user to evaluate the financial viability of process design concepts in minutes, so that to get early, detailed answers to the important questions of "How much?", "How long?" and, most importantly, "Why?" Aspen IPE has the following main features: links to process simulator software programs, mapping of simulator models to process equipment types, sizing of equipment, capital investment and schedules, development of operating costs, investment analysis, etc.

In Taylor *et al.*'s (2000) study, a dry-grind process for fuel ethanol production by continuous fermentation and stripping was created using Aspen Plus (Aspen Technology, Cambridge, MA). Simulation and cost evaluation results showed that substitution of continuous fermentation and stripping for continuous cascade fermentors result in an overall cost savings of $0.03 per gallon of ethanol produced. The savings are due primarily to approximately 50% higher solids concentrations, reducing the load on byproduct dewatering equipment and lowering the total capital investment by over $1,000,000. With some modifications, the process may show greater savings at higher solids concentrations.

In Wingren *et al.*'s (2003) study, in order to perform techno-economic evaluation of producing ethanol from softwood by means of comparison of simultaneous saccharification and fermentation (SSF) process and separate hydrolysis and fermentation (SHF) process, Aspen Plus was also used for process modeling to solve the mass and energy balances and to calculate the thermodynamic properties of the streams involved in the process. The capital costs were estimated using Aspen IPE. As a result of this simulation, the unit production cost of ethanol was estimated to be 0.57 $/kg for the SSF process and 0.63 $/kg for the SHF process.

2.3 Knowledge gap

Even though many process simulations of ethanol production have been studied as mentioned above, and a lot of studies about VHG fermentations have been carried out, simulation of a complete VHG fermentation process has not been reported so far. Since VHG fermentation is getting much more popular because of the high ethanol productivity (Lin, *et al.*, 2003), and process modeling has its advantage to save time and money before making capital investment decisions, simulations of VHG fermentation conditions were carried out and analyzed in this study. Economical evaluations of the VHG fermentation conditions comparing with other fermentation conditions will give us some suggestions on future studies on ethanol fermentation.

It should also be mentioned that, in the previous reviewed studies, process models were mostly used to simulate one isolated process with high stability. Most simulation parameters and reaction conditions were defined at a fixed value and remained unchanged throughout the whole simulation, except one parameter was changed only for sensitivity analysis. However, since we want to investigate the effects of both glucose feeding concentration and redox potential control on ethanol fermentation, combinations of different levels of glucose feeding concentrations and redox potential control settings were applied (9 scenarios in total). Due to the application of process simulation, different fermentation scenarios performed under different lab fermentation conditions can be all incorporated into the same model with only necessary modifications on a few model parameters (reaction extents, starch content in feed, reaction coefficients, etc.). In this way, evaluation results of each applied scenario can be obtained within a comparably short period, and all these data can be compared and analyzed, both technically and economically.

CHAPTER 3 MATERIALS AND METHODS

3.1 Experimental data collection

Redox potential-controlled fermentation measurements were previously reported by Lin *et al.* (2010). All data used for simulations in this study were measured by Lin *et al.* (2010). Fermentation data was shown in Appendix A. Briefly, an industrial *S. cerevisiae* strain (Ethanol Red^{TM} obtained from the Lesaffre Yeast Corp. Milwaukee, MI, USA) was pre-cultured overnight and cultivated in a jar fermentor with 1-liter working volume (model: Omni culture fermentor, New York, NY, USA). Each fermentor was equipped with an autoclavable redox potential electrode that was custom-made and ordered through Cole-Palmer Inc. (12 mm × 250 mm, Vernon Hills, IL, USA). Data were acquired by using LabView (Version 8.5, National Instrument, Austin, TX, USA), and a PID control algorithm was implemented to control redox potential at a desired level. The agitation rate was kept at 150 rpm for all runs. When the measured redox potential becomes lower than the set-point value, sterilized air was provided to fermentor to raise redox potential to the desired level. Fermentation broth was sampled every 6h. An HPLC equipped with an RI detector was used to automatically quantify the residual glucose, ethanol, and other metabolites.

3.2 Simulation software

The first simplified simulation model was established using Superpro Designer v7.0 (Intelligen, INC. 2326 Morse Avenue, Scotch Plains, NJ07076, USA). Physical properties of the components were obtained from Superpro Designer databank. Material and energy balances and economic calculations can be both performed by Superpro Designer v7.0.

The second and more accurate simulation model was created using Aspen Plus 2006 (Aspen Technology, Inc. 200 Wheeler Road, Burlington, Massachusetts 01803, USA). Physical properties of the components involved in this study were either obtained from Aspen Plus 2006 databank or defined by user according to literature or experimental data. Material and energy balance calculations were performed by Aspen Plus 2006, economical evaluation of the process model was carried out by Aspen Icarus Process Evaluator 2006 (Aspen Technology, Inc. 200 Wheeler Road, Burlington, Massachusetts 01803, USA).

Table 1 lists costs used in the economic evaluation of both models. Since results of economical evaluations are quite sensitive to these cost values, especially for raw materials (glucose in the Superpro model and corn in the Aspen Plus model) and the main product ethanol, the purchasing price of corn used is the average value of last six months' price (from September 2010 to February 2011) obtained from "Index Mundi" (http://www.indexmundi.com/commodities/, March 13th, 2011); selling prices of ethanol and DDGS used, as well as purchasing price of glucose (dextrose), are also the average values of last six months' price (from September 2010 to February 2011) according to Economic Research Service of United States Department of Agriculture (ERS/USDA); other costs were obtained from literature or online searching. All cost values presented in this study are in US dollars.

Table 1 Costs used in economic evaluation.

	Purchasing price ($/kg)	Selling price ($/kg)
Raw materials		
Corn	0.248183	
Glucose	0.636034	
Water	0.000044	
Acid	0.153000	
α-Amylase	2.250000	
Urea	0.353020	
Yeast	5.510000	
Products		
Ethanol		0.724419
Dry DDGS		0.175334
Proteins		0.373890
CO_2		0.015940

In addition, the selling price of the byproduct stream DDGS (Dried Distillers Grains with Solubles) in the Superpro model was calculated based on its protein content, and the selling price of the byproduct stream DDGS in the Aspen Plus model was calculated according to the stream's moisture content, according to each model's stream definition.

3.3 General process and design data

The annual production rate of models is considered to be 85~150 million kg ethanol per year, depending on the feeding glucose concentration to the fermentor. The annual operating time of the plant is designed to be 7920 hours (330 days). Building materials of process equipments are defined according to literatures or default of software databank.

3.4 Superpro model

3.4.1 Process description

The process flow diagram (PFD) used in this study is shown in Figure 1. This Superpro model used in this study was simplified and modified from Kwiatkowski *et al.* (2006), which is shown in Figure 2. Only fermentation and ethanol separation sections were modeled in this model. Therefore different process feed was also used (glucose instead of corn). Parameters used during process simulation and economic evaluation are based on Kwiatkowski *et al*.'s (2006) model or experimental data collected in our laboratories (Lin *et al*., 2010), and model setting are provided in section 3.4.2 "Economic evaluation". This simulation focused on comparing and studying the technical and economical effects of the initial glucose concentration and redox potential settings on ethanol production under VHG conditions.

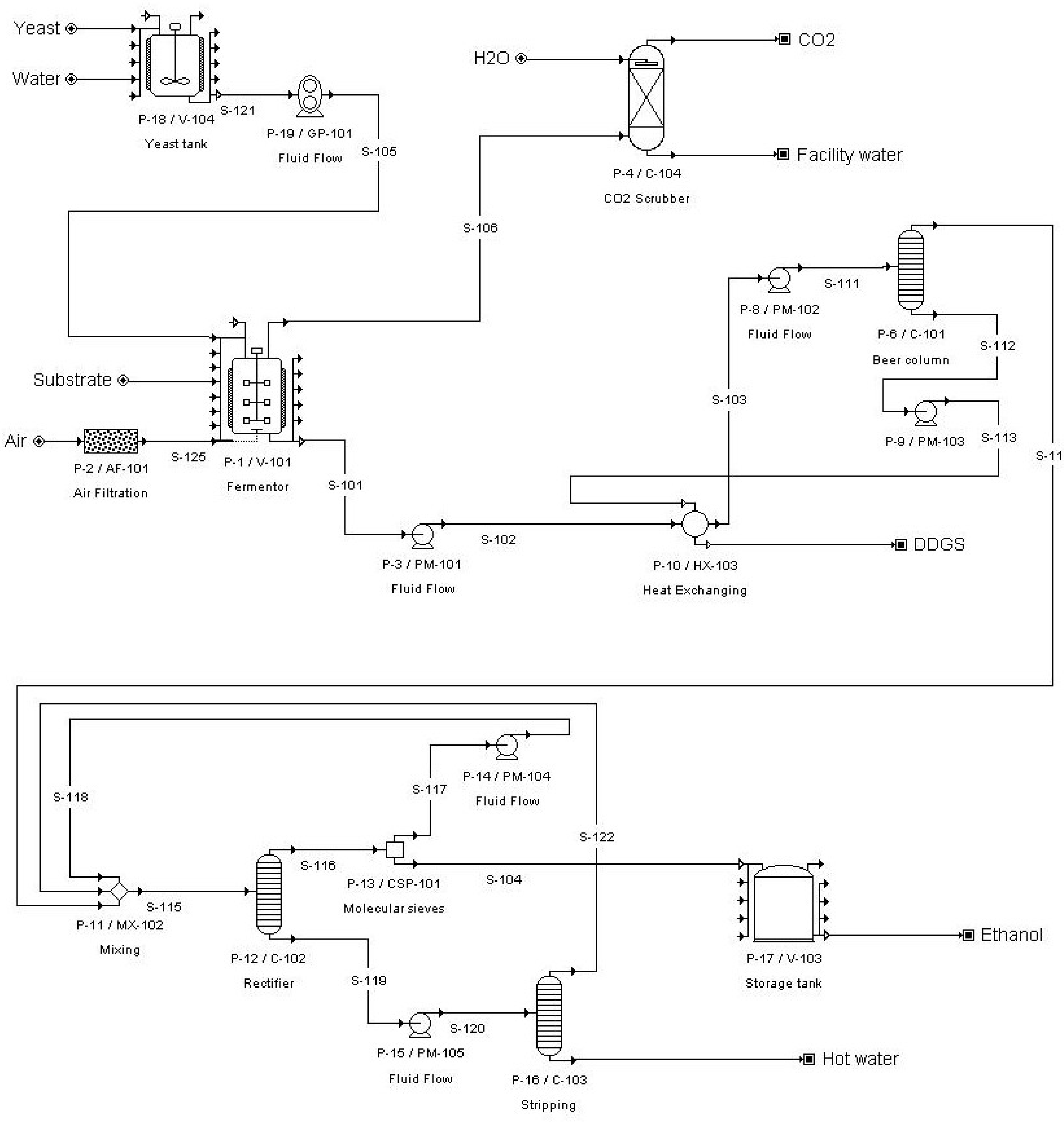

Figure 1 Superpro process model for redox potential-controlled very-high-gravity ethanol fermentation (simplified from Kwiatkowski *et al.* (2006)).

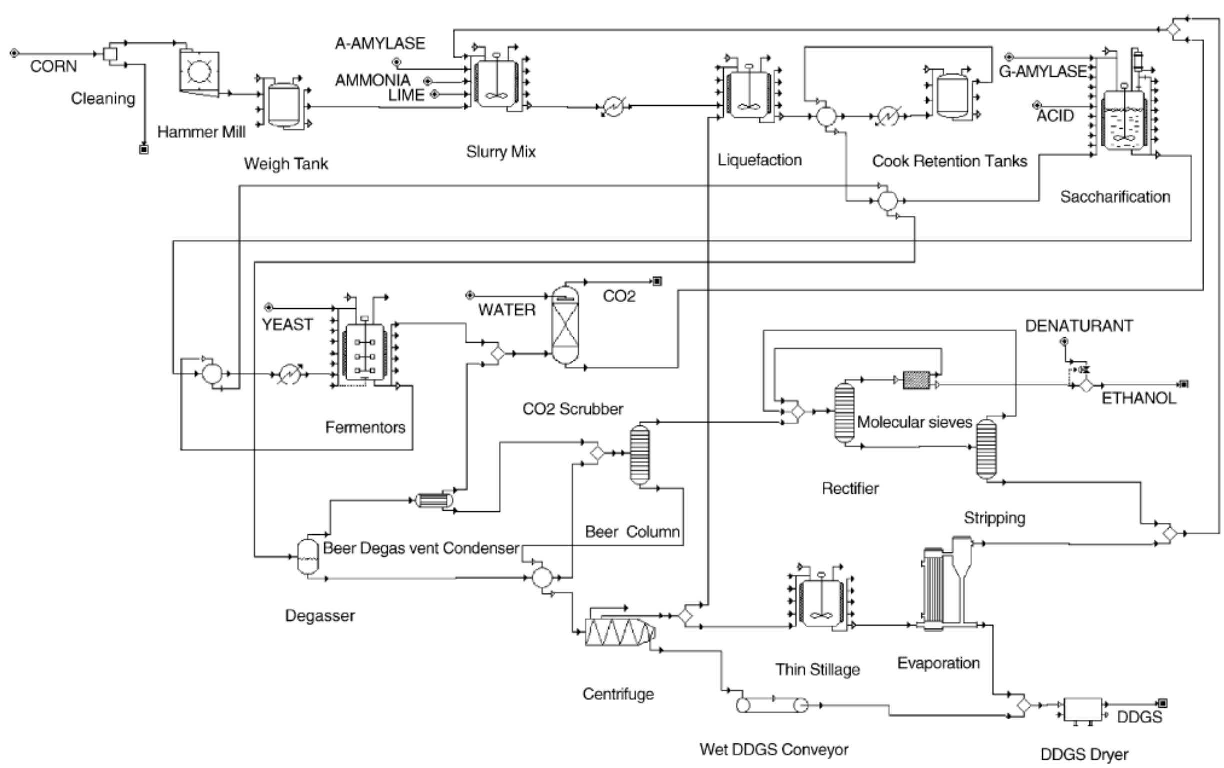

Figure 2 Simplified PFD of the original dry-grind ethanol from corn process (Kwiatkowski *et al.* (2006)).

Since the Superpro version used in this study has a number limitation of unit procedures that can be used in an individual process model, and this simulation focused on studying the technical and economical effects of the glucose feed and redox potential control on ethanol production under VHG conditions, therefore the milling, liquefaction and saccharification processes were purposely ignored, as well as the downstream treatment procedures of the raw DDGS stream. In this way, only necessary components for the simplified model were registered. The modified model starts from the Fermentor and focuses only on separation of the main product ethanol. To approximate the composition of the output stream of the liquefaction and saccharification processes which is then used as the feed of fermentation process, certain ingredients were added as components into the feed stream (oil, non-fermentable solids, non-fermentable saccharides, proteins, etc). However, the main variation of the feed's composition, and also the major factor that affects the results of economic evaluation, is the glucose feeding concentration, which was studied in three levels as described in Table 2. The fluctuation in feed listed in Table 2, 300±6.42 for example, stands for the deviation of measured values determined by HPLC. For each applied condition, only one input value was used for the certain parameter.

Table 2 Glucose concentration in feed (substrate of fermentation).

Conditions	Concentration of glucose in feed (g/L)
A	300±6.42
B	250±3.95
C	200±4.99

In the Superpro model, two reactions are defined in the fermentor:

$$\text{Glucose} \rightarrow \alpha\ \text{Carbon Dioxide} + \alpha\ \text{Ethyl Alcohol} + \beta\ \text{Yeast Dry Matter} \tag{1}$$

$$\text{Yeast Dry Matter} \rightarrow 0.55\ \text{Other Solids} + 0.45\ \text{Protein Soluble} \tag{2}$$

In which α, β in Equation 1 are the molar coefficients of the first reaction that were determined based on results of lab fermentation experiments before simulation. Whereas 0.45 and 0.55 in Equation 2 are predefined mass coefficients according to Kwiatkowski *et al* (2006).

The output stream of the fermentor is preheated in a heat exchanger right before being pumped into the distillation section. The distillation section consists of a beer column, connected with a rectifier and a stripper. The beer column is a primary separation process unit to separate most of ethanol (over 99% ethanol in the feed stream) from the fermentor's output stream together with a small amount of water. The rectifier and stripper are distillation units for further ethanol-water separation. Stage efficiencies of the beer column, rectifier and stripper are 36.4%, 40% and 40% according to Kwiatkowski *et al* (2006), respectively.

The bottom stream of the beer column is sent to a heat exchanger as a heating agent, and then will be treated and dried to produce distiller's dry grains with solubles (DDGS), which is another revenue stream other than the main product stream. It should be mentioned that since glucose was directly used as the fermentation substrate instead of liquefaction and saccharification product from corn or sugarcane, the composition of the yielding DDGS stream is different from the actual byproduct DDGS, the main protein content is biomass instead of proteins from corn or sugarcane.

In order to overcome the limitation of distillation process to yield main product stream with high ethanol concentration, molecular sieves are applied to separate the azeotrope of water and ethanol (94.68% ethanol, v/v), so that ethanol concentration reaches over 99.5% in the final product stream.

In the Superpro model, CO_2 produced during the fermentation process is assumed to be sold as byproduct from exhaust of the CO_2 scrubber. The CO_2 stream can also be captured and compressed or transported to deep injection sites with pipelines, these options will be discussed later in section 4.4 "Disposal of CO_2 produced during fermentation".

3.4.2 Economic evaluation

3.4.2.1 Economic evaluation parameters

Input and output of the model are shown in Figure 3. After the model was completed with all required settings (blocks, stream, components, etc), parameters (glucose feeding concentration, reaction extent and reaction coefficients) calculated from results of different applied fermentation conditions were applied to the model as the input, the model was then run to perform mass and energy balance, as well as economic evaluations to obtain all the output required (Annual production rate, product sales, unit production cost, etc) for analysis in this study.

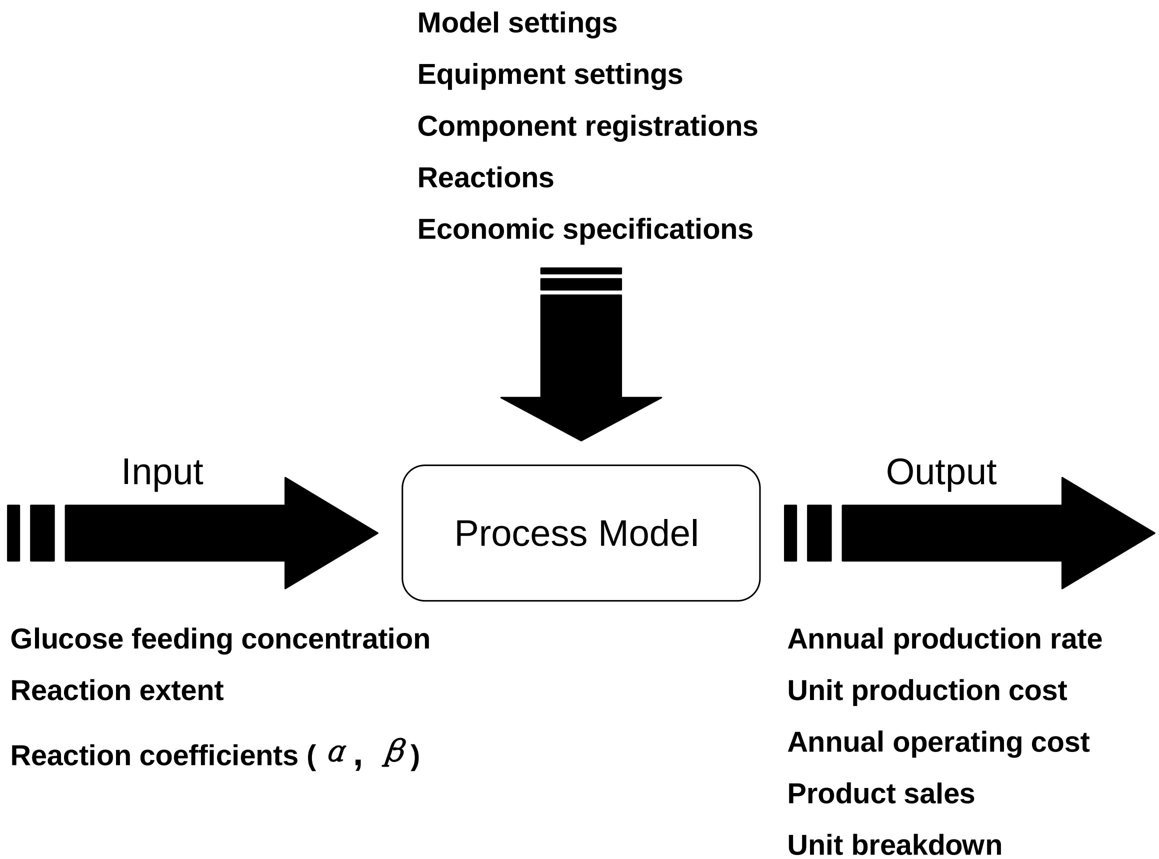

Figure 3 Model input and output. Only outputs used in comparison and discussion were presented.

The economic evaluation parameters for the entire process are listed in Table 3:

Table 3 Entire process economic evaluation parameters in Superpro model.

Item	Value	Unit
Time parameters		
Year of analysis	2010	
Year construction starts	2010	
Construction period	12	Months
Startup period	1	Months
Project lifetime	15	Years
Inflation	4	%
NPV interest		
Low	7	%
Medium	9	%
High	11	%
Operating unit costs		
Labor		
Operator	30	$/Hour
Supervisor	50	$/Hour
Utilities		
Chilled water	0.40	$/Mt
Cooling water	0.05	$/Mt
Steam	12.00	$/Mt
Steam (High pressure)	20.00	$/Mt

3.4.2.2 Components and streams

The following components were registered before creating the model:

Table 4 Component registration for Superpro model.

Name	MW (g/gmol)
Water	18.02
Dry Yeast	180.16
Non-starch Polysaccharides	18.02
Oil	18.02
Other Solids	18.02
Yeast Dry Matter	18.02
Protein-insoluble	180.16
Protein-soluble	180.16
Ethanol	46.07
CO_2	44.01

In this model, Ethanol, DDGS and CO_2 were classified as revenue streams, and all input streams were classified as raw material streams. Purchasing price of raw material streams and selling price of revenue streams were calculated according to the contents' prices, except for Ethanol and CO_2, the selling prices were set to 0.724419 \$/kg and 0.011955 \$/kg, respectively, as listed in Table 1.

3.4.2.3 Equipment sizing

Yeast tank The Yeast tank is a continuous storage blending tank in Superpro Designer's databank. The final temperature was set to 42.34℃, and the pressure is 1.013 bar. The specific power consumption was set to 0.5 kW/m^3. The residence time of the Yeast tank was set to 40 h, with a 90% working volume of 2669.34 L. Working volume ranges from 15~90% of the total volume. The Volume of the tank is 2.97 m^3, with a height of 3.24 m and diameter of 1.08 m.

Yeast pump The fermentor yeast pump has a pressure change of 150 psi and a calculated volumetric flow rate of 0.06716 m^3/h. The operating power is 0.055 kW and the efficiency is 35%.

Air filter The Air filter is an air filtration unit in Superpro Designer's databank with an air flow of 4600.369 m^3/h. The size is calculated automatically by Superpro Designer according to the design flow rate.

Fermentor The fermentor is a continuous stoichiometric fermentor in Superpro Designer's databank. The fermentor was operated under 30 ℃ and atmospheric pressure, with a specific power consumption of 0.028 kW/m^3, and an aeration rate of 0.01 VVM. The residence time varied according to different fermentation conditions applied. The working volume is set to 83% of the total volume. 98.5% of CO_2, 2.55% of ethanol and 0.23% water was emitted from the fermentor. The fermentor is 29.8 m in height and 19.9 m in diameter, and the maximum volume is 14000 m^3.

CO_2 scrubber The CO_2 scrubber is an absorption unit in Superpro Designer's databank. It was designed to remove 99.8% dry yeast, 0.1% CO_2 and 59% water from the feed. The design component is ethanol, diffusivity in gas phase is 123 cm^2/s, and 13 cm^2/s in liquid phase. The CF was set to be 155, with the total specific surface of 190 m^2/m^3, nominal diameter of 0.00762 m, and critical surface tension of 40 dyn/cm. The column is 8.571 m in height and 1.411 in diameter.

Beer pump The beer yeast pump has a pressure change of 50 psi and a calculated volumetric flow rate of 137.409 m^3/h. The operating power is 18.798 kW and the efficiency is 70%.

Heat exchanger The heat exchanger has a countercurrent flow type with a correction factor of 1.00. The heat transfer coefficient was set to 140 btu/h-ft^2-℃. The cold stream outlet temperature was set to 95 ℃, and the minimum achievable temperature is 5 ℃. The maximum heat transfer surface was set to 929.03 m^2 and the exchanger type is plate and frame.

Beer column feed pump The beer column feed pump has a pressure change of 45 psi and a calculated volumetric flow rate of 117.449 m^3/h. The operating power is 14.460 kW and the efficiency is 70%.

Beer column The beer column is a distillation unit in Superpro Designer's databank. It was designed to separate 100% CO_2, 99.7% ethanol and 12.44% water from the beer. The reflux ratio was calculated to be 0.121. The column pressure was set to 1.03 bar and vapor linear velocity was set to 1.618 m/s. The stage efficiency was set to 36.4%. The condenser is operated at 104 ℃ and the Reboiler is operated at 115.33 ℃. The column is 15.545 m in height and 2.803 m in diameter with a stage height of 0.457 m and the design pressure of 1.48 atm.

DDGS pump The DDGS pump has a pressure change of 50 psi and a calculated volumetric flow rate of 106.221 m^3/h. The operating power is 14.531 kW and the efficiency is 70%.

Stream mixer The stream mixer is a 3-stream mixing unit in Superpro Designer's databank. The calculated operating mass flow rate is 36233.63 kg/h.

Rectifier The rectifier is a distillation unit in Superpro Designer's databank. It was designed to separate 99.44% ethanol and 11.46% water from the feed. The reflux ratio was calculated to be 0.126. The column pressure was set to 1.03 bar and vapor linear velocity was set to 0.678 m/s. The stage efficiency was set to 40%. The condenser is operated at 95 ℃ and the Reboiler is operated at 114.36 ℃. The column is 16.612 m in height and 3.153 m in diameter with a stage height of 0.593 m and the design pressure of 2 bar.

Molecular sieves The rectifier is a 2-way component splitting unit in Superpro Designer's databank. It was designed to split 16.2% ethanol and 97% water from the feed to the top stream. The operating power was set to 14.4 kW.

Recycle pump The recycle pump has a pressure change of 50 psi and a calculated volumetric flow rate of 1.712 m^3/h. The operating power is 0.234 kW and the efficiency is 70%.

Stripper feed pump The stripper feed pump has a pressure change of 50 psi and a calculated volumetric flow rate of 13.904 m^3/h. The operating power is 1.902 kW and the efficiency is 70%.

Stripper The stripper is a distillation unit in Superpro Designer's databank. It was designed to separate 99% ethanol and 11.46% water from the feed. The reflux ratio was calculated to be 0.125. The column pressure was set to 1.03 bar and vapor linear velocity was set to 3 m/s. The stage efficiency was set to 40%. The condenser is operated at 90 ℃ and the Reboiler is operated at 114 ℃. The column is 12.344 m in height and 0.590 m in diameter with a stage height of 0.457 m and the design pressure of 1.5 bar.

Storage tank The storage tank is a continuous storage flat bottom tank in Superpro Designer's databank. The final temperature was set to 42℃, and the pressure is 1.013 bar. It has a 90% working volume of 433251 L. Working volume ranges from 15~90% of the total volume. The Volume of the tank is 481.39 m^3, with a height of 13.484 m and diameter of 6.742 m.

3.4.2.4 Purchase cost of equipments

Purchase costs as well as required parameters were presented in Table 5:

Table 5 Parameters for the calculation of equipment purchase cost. In Material column, CS stands for Carbon Steel, SS304 stands for Stainless Steel 304, SS316 stands for Stainless Steel 316.

Equipment name	Cost estimation option	Material	Material factor	Installation cost (× PC)
V-104 (Yeast tank)	User-defined model	SS304	1.00	2.00
GP-101 (Yeast pump)	Set by user	SS316	1.00	2.00
AF-101 (Air filter)	Built-in model	CS	1.00	2.00
V-101 (Fermentor)	User-defined model	SS316	1.00	2.00
C-104 (CO_2 scrubber)	User-defined model	SS304	2.40	2.00
PM-101 (Beer pump)	Set by user	SS316	1.00	2.00
HX-103 (Heat exchanger)	User-defined model	CS	1.00	0.50
PM-102 (Beer column feed pump)	Set by user	SS316	2.05	2.00
C-101 (Beer column)	User-defined model	SS304	3.88	2.00
PM-103 (DDGS pump)	Set by user	SS316	2.05	2.00
MX-102 (Stream mixer)	Built-in model	CS	1.00	2.00
C-102 (Rectifier)	User-defined model	SS304	1.00	2.00
CSP-101 (Molecular sieves)	User-defined model	CS	1.00	2.00
PM-104 (Recycle pump)	Set by user	SS316	2.05	2.00
PM-105 (Stripper feed pump)	Set by user	SS316	2.05	2.00
C-103 (Stripper)	User-defined model	SS304	3.86	2.00
V-103 (Storage tank)	User-defined model	SS304	1.00	2.00

For the cost estimation option:

1. Set by user means you can specify the purchase cost yourself;

2. Built-in model is specific to this type of equipment;

3. User-defined model means you can define the parameters of a power-law model that will determine the cost of the equipment.

It should be mentioned that all the costs were calculated for the reference year of 2010. The user-specified cost can either be fixed and independent of the year of analysis for the design case or adjustable to inflation according to a reference year.

The user-defined cost model is of the following power-law form:

$$PC = C_o \left(\frac{Q}{Q_o} \right)^a \tag{3}$$

Where C_o is the base cost, Q_o is the base capacity, and a is the exponent of the power law function. In cases where the capacity variable Q needs to span a wide range of values, the total range is broken down into several intervals and a set of parameters a, C_o and Q_o is supplied for each interval. The specification of a user-defined cost model must also be accompanied by the calendar year (the reference year 2010 were used for this model) for which the cost estimates of the model are accurate, in order for the program to be able to adjust for inflation. Parameters of each unit procedure for the purchase cost model are listed in Table 6:

Table 6 Parameters of unit procedures for which the user-defined model was used to determine the purchase cost in Superpro Model.

Equipment name	Low end (m^3)	High end (m^3)	Q_o (m^3)	Base cost ($)	a
V-104 (Yeast tank)	0	1000	2.97	114700	0.6
V-101 (Fermentor)	100	14000	10446.31	2811200	0.6
C-104 (CO_2 scrubber)	0	10000	13.41	91300	0.6
HX-103 (Heat exchanger)	0	1000	402.34	458900	0.6
C-101 (Beer column)	0	50000	96.57	597000	0.6
C-102 (Rectifier)	1	10000	113.57	254000	0.6
CSP-101 (Molecular sieves)	10000	720000	22924.40	1717700	0.6
C-103 (Stripper)	0	100	3.72	168200	0.6
V-103 (Storage tank)	0	1000	481.39	93400	0.6

For example, the fermentor has a volume of 9237.69 m^3, then its purchase cost can be calculated as following:

$$PC_{Fermentor} = 2811200 \times \left(\frac{9237.69}{10446.31} \right)^{0.6} = 2611000\$.$$

3.4.2.5 Profitability calculations

In profitability analysis, the following items that are essential for economic analysis were calculated:

Annual production rate = Production rate × Annual operating time;

Annual operating cost = Raw materials cost + Labor cost + Facility cost + Utilities cost;

$$\text{Unit production cost} = \frac{\text{Annual operating cost}}{\text{Annual production rate}};$$

$$\text{Total product sales} = \sum_i (\text{Selling price}_i \times \text{Annual production rate}_i),\ (i = \text{Ethanol, DDGS, } CO_2);$$

$$\text{Cost breakdown}_i = \text{Unit production cost} \times \frac{\text{Cost}_i}{\text{Annual operating cost}},$$ (i = raw materials, labor, facility, utilities);

$$\text{Ethanol yield} = \frac{\text{Final ethanol concentration}}{\text{Initial glucose concentration - Final glucose concentration}};$$

For example, in the first repeat of condition Aa (Aa1):

Annual production rate = 17644.098 kg/h × 7920 h = 139741258.989 kg ethanol/year;

Annual operating cost = 218743308 \$ + 1980000 \$ + 9071000 \$ + 10192335 \$ = 239986643 \$;

$$\text{Unit production cost} = \frac{239986643\ \$}{139741258.989\ \text{kg ethanol}} = 1.7174\ \$/\text{kg ethanol};$$

Total product sales = 0.724419 \$/kg ×139741258.99 kg/year + 0.022417 \$/kg × 813729597.12

kg/year + 0.011955 \$/kg ×184208737.68 kg/year = 121674814.93 \$/year;

Cost breakdown of ethanol = 1.7174 \$/kg $\times \frac{218743308\ \$}{239986643\ \$}$ = 1.5653 \$/kg;

Ethanol yield = $\frac{125.95\ \text{g/L}}{302.15\ \text{g/L} - 15.37\ \text{g/L}}$ = 0.4392.

It should be noticed that values presented in next chapter is the average of two repeats of one certain condition.

3.5 Aspen Plus model

3.5.1 Process description

As mentioned before, since the academic version of Superpro Designer v7.0 used in the first model has a disadvantage that the number of unit procedures is limited to be less than 25 in one process model, therefore the liquefaction and saccharification sections of an ethanol producing were purposely ignored, as well as downstream treatment of DDGS stream and recycle streams. Also, glucose, an important intermediate product produced from the saccharification section and consumed in the fermentation section, is directly used as process feed of the entire model. This makes the estimated costs too high to be compared with market values. In order to perform the process simulation in a more accurate model, Aspen Plus was introduced to create a model of an entire ethanol fermentation process.

A brief demonstration of the Aspen Plus process model used in this study is shown in Figure 4, The PFD of this model is shown in Appendix B. The original model was created based on Taylor *et al*. (2000). Some alternative branches in the original model for possible future scale-up or scale-down were deleted, only necessary components for this study was included or created. Model settings used for process simulation and economic evaluation were determined based on Taylor *et al*.'s (2000) model or from experimental data collected in laboratories (Lin *et al*., 2010), and are listed in Appendix C. This simulation focused on studying the technical and economical effects of the glucose feeding concentration and redox potential control on the ethanol production under VHG conditions, and the estimated unit production cost of ethanol can also be compared with market price.

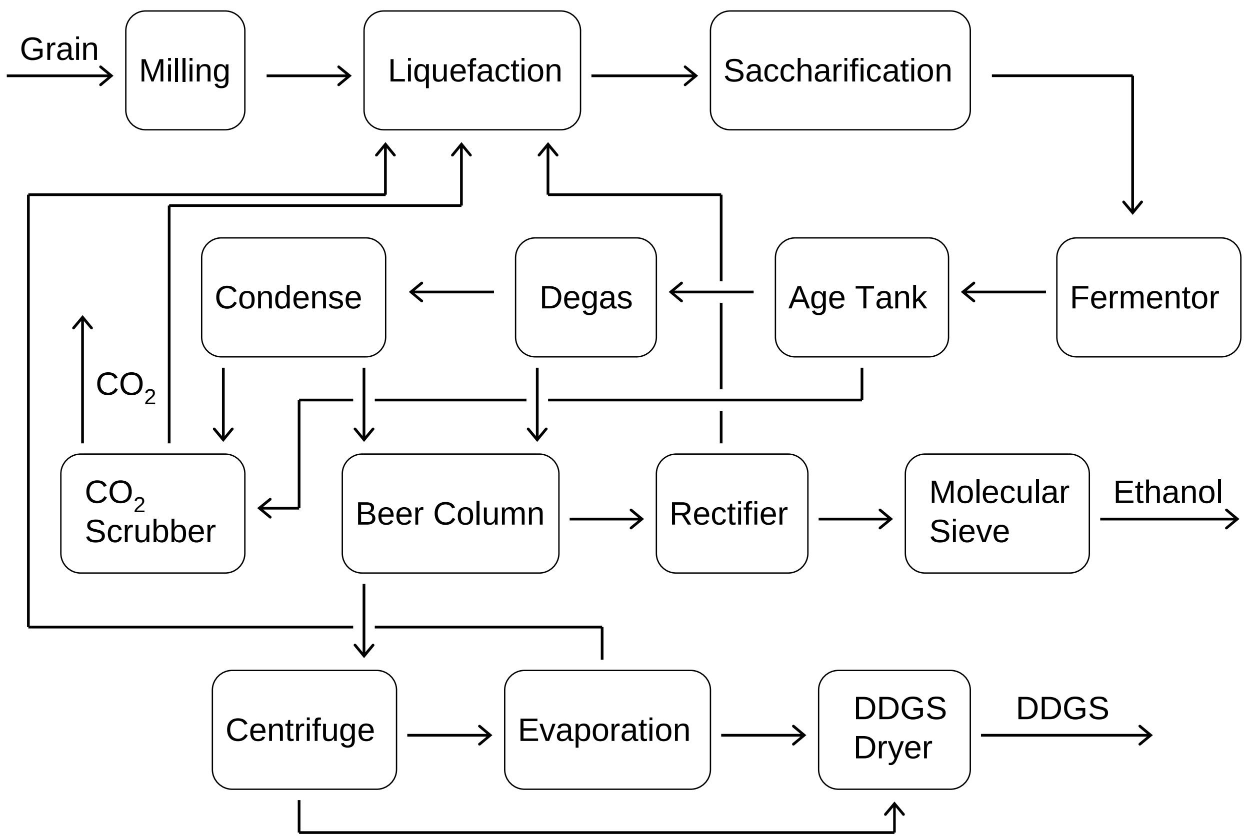

Figure 4 Aspen Plus process model for redox potential-controlled very-high-gravity ethanol fermentation (modified from Taylor *et al*. (2000))

The same experimental conditions were applied in this model for simulation in order to compare the two models. The glucose concentration in the feed to fermentor was shown in Table 2, the same conditions were applied in the previous Superpro model.

In this model, the glucose concentration in the feed of fermentor was manipulated by varying the starch content in the Grain stream feeding to the Milling module as shown in Figure 4. The Milling module is a separation process while the Liquefaction module is a heating process, in both of which no chemical reactions were defined. However, in the Saccharification module, one reaction was defined:

$$\text{Starch} + \text{Water} \rightarrow \text{Glucose} \tag{4}$$

Equation 4 defined the molecular relation of the reaction from starch to glucose, which means one molecule of starch one molecule of water generates one molecule of glucose. Starch in this model is a predefined pure component with a molecular weight of 162.14.

In the fermentor, two reactions were defined:

$$\text{Glucose} \rightarrow \alpha\,\text{CO}_2 + \alpha\,\text{Ethanol} + \beta\,\text{YDM} \tag{5}$$

$$\text{YDM} \rightarrow 1.13635848\,\text{Protein} \tag{6}$$

α, β in Equation 5 are the molar coefficients of the first reaction that were determined based on results of lab fermentation experiments before simulation, as described in 3.3.1 "Process modeling using Superpro Designer v7.0". Whereas 1.13635848 in Equation 6 is the predefined mass coefficient according to predefined molecular weights of the components YDM and Protein. YDM in Equation 5 and Equation 6 is short for Yeast Dry Matter.

After fermentation, the beer is sent to an aging tank, where most of CO_2 (over 98.7% in feed) is separated from the beer, and then is sent into a degasser where CO_2 in the beer is further removed (70% of the left over CO_2 in the beer). After that, the beer is sent into the distillation section which includes a beer column and a rectifier. The top output stream of the degasser is condensed by a condenser in order to recover most of ethanol (around 80% in feed) in it. This condensed stream is also sent to the beer column for further separation.

The beer column is a primary separation process unit to separate most of ethanol (over 99.7% of ethanol in its feed stream) from the fermentor's output stream together with a certain amount of water. This stream which is mainly composed of ethanol and water is then sent to a rectifier connected with a molecular sieve for further ethanol-water separation. The using of molecular sieve is to overcome the limitation of distillation process to yield main product stream with high ethanol concentration. Molecular sieves are applied to separate the azeotrope of water and ethanol (ethanol : water = 95.6 : 4.4 in mass), with recycling, ethanol concentration in the output stream reaches to over 99.25% in mass.

The bottom stream of the beer column is sent to a centrifuge and then a dryer to yield DDGS, which is the main byproduct of this ethanol producing process. It should be mentioned that under actual circumstances, protein and other solids contents in the feed stream to the Milling section are proportionally changed while varying the starch content. However, since variations of protein and other solids contents in the feed stream have no significant influence on economical evaluation results, they remained unchanged in simulated scenarios in order to precisely manipulate the glucose concentration in feed stream of the fermentor.

The top output streams of the aging tank and condenser which are rich in CO_2 are sent to a CO_2 scrubber where liquid portion of the feeds are absorbed by water and major portion of CO_2 (over 99.8%) produced during the fermentation process is gathered for further emission, capture or deep injection.

In the Aspen Plus model, CO_2 produced during the fermentation process is assumed to be captured after treatment in the CO_2 scrubber and sold as another byproduct.

3.5.2 Economic evaluation

3.5.2.1 Economic evaluation parameters defined in Aspen IPE

Since Aspen Plus can not directly perform economic evaluations itself, another Aspen software was introduced. To perform economic evaluation for a existed process model after the simulation was correctly completed, simulation results were sent to Aspen IPE for economic evaluations, and required or default parameters were shown in the following tables:

Table 7 Investment parameters used in Aspen Plus model.

Name	Values	Units
INVESTMENT PARAMETERS		
Project Capital Escalation	5	Percent/Period
Products Escalation	5	Percent/Period
Raw Material Escalation	3.5	Percent/Period
Operating and Maintenance Labor Escalation	3	Percent/Period
Utilities Escalation	3	Percent/Period
PROJECT CAPITAL PARAMETERS		
Working Capital Percentage	5	Percent/Period
OPERATING COSTS PARAMETERS		
Operating Supplies	25	Cost/Period
Laboratory Charges	25	Cost/Period
Operating Charges	25	Percent/Period
Plant Overhead	50	Percent/Period
G and A Expenses	8	Percent/Period
FACILITY OPERATION PARAMETERS		
Facility type	Chemical Processing Facility	
Operating mode	Continuous Processing - 24 Hours/Day	
Length of Start-up Period	20	Weeks
Operating Hours per Period	7920	Hours/Period
Process Fluids	Liquids and Solids	

Table 8 Operating unit costs defined in evaluating the Aspen Plus model.

Name	Values	Units
LABOR UNIT COSTS		
Operator	20	Cost/Operator/Hour
Supervisor	35	Cost/Supervisor/Hour
UTILITY UNIT COSTS		
Electricity	0.0354	Cost/KWH
Potable Water	0	Cost/M3
Fuel	0.002427	Cost/MEGAWH
Instrument Air	0	Cost/M3

Table 9 General specifications defined in evaluating the Aspen Plus model.

Name	Settings
Process Description	Proven process
Process Complexity	Typical
Process Control	Digital
PROJECT INFORMATION	
Project Location	North America
Project Type	Grass roots/Clear field
Contingency Percent	18
Estimated Start Day of Basic Engineering	1
Estimated Start Month of Basic Engineering	JAN
Estimated Start Year of Basic Engineering	10
Soil Condition Around Site	SOFT CLAY
EQUIPMENT SPECIFICATION	
Pressure Vessel Design Code	ASME
Vessel Diameter Specification	ID
P and I Design Level	FULL

3.5.2.2 Components and streams

Components used in the Aspen Plus model is shown in Table 10:

Table 10 Component registration for Aspen Plus model.

Name	Molecular weight
Water	18.02
Ethanol	46.07
CO_2	44.01
Glucose	180.156
Starch	162.141
Protein	132.115
Oil	132.115
YDM	150.130
Cpoly	147.128

Three product streams were defined in Aspen IPE: Ethanol, DDGS and CO_2. Selling prices of product streams were calculated according to prices listed in Table 1.

3.5.2.3 Equipments

When creating the Aspen Plus model, operating conditions were defined, as well as some sizing information, and are shown in Appendix C. However, after simulation results were sent to Aspen IPE, equipment mapping and sizing can be automatically performed by Aspen IPE. In this study, default settings in Aspen IPE were used when performing equipment mapping and sizing, unless the required sizing information was already set in operating conditions.

3.5.2.4 Profitability calculations

Simulation results of Aspen Plus model used in this study were obtained using almost the same calculation methods as the Superpro model, except for the calculation of Annual operating cost:

Annual operation cost = Subtotal operating cost + G and A cost;

Subtotal operating cost = Total raw materials cost + Total utilities cost + Operating labor cost + Maintenance cost + Operating charges + Plant overhead;

G and A cost = 0.08 × Subtotal operating cost.

3.6 Reactions and coefficients

In simulation, different fermentation conditions were applied by manipulating the reaction coefficients *α, β* in Equation 1 and 5, as well as its reaction extent. *α* is the molar ratio of yield ethanol over depleted glucose that were measured by lab experiments under certain applied conditions, whereas *β* is dependent to *α* to ensure mass balance of the reaction.

1.13635848 in Equation 6 is in fact an approximate value of the fractional ratio of YDM and Protein' molecular weight, which are 150.130 and 132.115, respectively. Because a fraction can not be specified as reaction coefficients in a simulator.

The reaction extent of Equation 1 is the mass ratio of depleted glucose over total feed glucose measured under certain applied conditions. Reaction extent of Equation 2 and 6 is fixed to 0.6, according to Kwiatkowski *et al*.'s (2006). The reaction extent of Equation 5 was set to 0.99, according to Taylor *et al*. (2000).

CHAPTER 4 RESULTS AND DISCUSSION

By manipulating mass composition of glucose in feed of fermentor in both models, and applying different fermentation conditions to the two models, VHG fermentations were simulated by two process models. Though these fermentation conditions were only performed under laboratory experiments, therefore there might be some inaccuracies from the simulated scenarios to an actual VHG fermentation process, these results are still helpful for future studies on VHG fermentation. In addition, economical effects of different fermentation conditions were also compared based on economic evaluation results.

4.1 Experimental data and parameter calculation

The experimental data provided by Lin *et al.* (2010) that were used in process simulations were presented in Appendix A. To apply different fermentation conditions to the two models, certain calculations are required to convert these experimental data to model parameters. The calculations were briefly discussed in section “3.6 Reactions and coefficients”, calculated values that can be used as model parameters are shown in Table 11:

Table 11 Parameters evaluated from experimental data that are required in modeling. In the first column of scenarios, different glucose concentrations in feed stream are denoted as: A = 300±6.42 g/L, B = 250±3.95 g/L, C = 200±4.99 g/L. Different redox potential control levels are denoted as: a = no control, b = -150 mV, c = -100 mV. 1 and 2 stand for different repeats of an individual scenario.

Conditions	Residence time (h)	Reaction 1 (or 4) extent	α	β in reaction 1	β in reaction 4
Aa1	53	0.9491	1.7175	1.4123	0.1695
Aa2	53	0.9302	1.7966	1.0165	0.1220
Ab1	53	0.9350	1.7944	1.0280	0.1234
Ab2	53	0.9843	1.8635	0.6824	0.0819
Ac1	53	0.9226	1.6402	1.7988	0.2159
Ac2	53	0.9931	1.5775	2.1121	0.2535
Ba1	47	1	1.9884	0.0581	0.0070
Ba2	47	1	1.8950	0.5249	0.0630
Bb1	41	1	1.8907	0.5466	0.0656
Bb2	41	1	1.8905	0.5472	0.0657
Bc1	41	1	1.9202	0.3989	0.0479
Bc2	41	1	1.9588	0.2059	0.0247
Ca1	29	1	1.8244	0.8778	0.1054
Ca2	29	1	1.8186	0.9066	0.1088
Cb1	29	1	1.8787	0.6065	0.0728
Cb2	29	1	1.8122	0.9388	0.1127
Cc1	29	1	1.7683	1.1582	0.1390
Cc2	29	1	1.8399	0.8004	0.0961

For the condition "Aa1":

Residence time = Fermentation time + 5 hours (Maintenance and cleaning) = 48 + 5 = 53 hours;

Reaction 1 (or 4) extent

$$= \frac{\text{Initial glucose concentration - Final glucose concentration}}{\text{Initial glucose concentration}} = \frac{302.15 - 15.37}{302.15} = 0.9491;$$

$$\alpha = \frac{\text{Final ethanol concentration} / MW_{\text{Ethanol}}}{(\text{Initial glucose concentration - Final glucose concentration}) / MW_{\text{Glucose}}} = \frac{125.95 / 46.07}{(302.15 - 15.37) / 180.16}$$

$= 1.7175;$

$$\beta_{\text{Reaction 1}} = \frac{\text{MW}_{\text{Glucose}} - (\text{MW}_{\text{Ethanol}} + \text{MW}_{\text{CO}_2}) \times \alpha}{\text{MW}_{\text{Yeast Dry Matter}}} = \frac{180.16 - (46.07 + 44.01) \times 1.7175}{18.02} = 1.4123;$$

$$\beta_{\text{Reaction 4}} = \frac{\text{MW}_{\text{Glucose}} - (\text{MW}_{\text{Ethanol}} + \text{MW}_{\text{CO}_2}) \times \alpha}{\text{MW}_{\text{YDM}}} = \frac{180.16 - (46.07 + 44.01) \times 1.7175}{150.13} = 0.1695.$$

It should be mentioned that since β is dependent to α, therefore for each applied condition in one model, only one pair of α and β can be specified.

4.2 Results of process simulation using Superpro Designer v7.0

4.2.1 General results

In the process simulation, two variables are introduced: initial glucose concentration to the fermentor was obtained from experiments: 200±4.99, 250±3.95 and 300±6.42 g/L, along with different levels of redox potential control. The summarized results of economic evaluation are shown in Table 12. The breakdown of unit production cost for each basic case is shown in Table 13. The annual operating cost in Table 12 is composed of raw materials, facility, labor and utility, as listed in the first column of Table 13. As for one experimental condition, two repeats were applied, therefore evaluation results discussed in following parts of this chapter were actually averages of the two repeats' estimated values.

Table 12 General results of economic evaluation. Different glucose concentrations in feed stream are denoted as: A = 300±6.42 g/L, B = 250±3.95 g/L, C = 200±4.99 g/L. Different redox potential control levels are denoted as: a = no control, b = -150 mV, c = -100 mV.

	Production rate (10^6 kg ethanol/year)	Unit production cost ($/kg ethanol)	Annual operation cost (10^6 $/year)	Total product sales (million $/year)
Aa	141.53	1.697	240.11	122.30
Ab	149.96	1.608	240.61	127.51
Ac	131.94	1.817	239.63	117.80
Ba	139.79	1.467	204.92	117.85
Bb	135.85	1.504	204.34	115.68
Bc	139.43	1.467	204.56	117.60
Ca	105.85	1.573	166.51	93.85
Cb	107.00	1.558	166.60	94.47
Cc	104.69	1.591	166.45	93.24

Table 13 Breakdown of unit production cost for basic cases; all values in $/kg Ethanol. Different glucose concentrations in feed stream are denoted as: A = 300±6.42 g/L, B = 250±3.95 g/L, C = 200±4.99 g/L. Different redox potential control levels are denoted as: a = no control, b = -150 mV, c = -100 mV.

Cost item ($/kg MP)	Aa	Ab	Ac	Ba	Bb	Bc	Ca	Cb	Cc
Raw materials	1.546	1.462	1.658	1.315	1.352	1.318	1.399	1.384	1.415
Facility	0.065	0.062	0.069	0.064	0.063	0.062	0.071	0.071	0.072
Labor	0.014	0.014	0.015	0.014	0.015	0.014	0.019	0.019	0.019
Utility	0.073	0.071	0.075	0.075	0.075	0.074	0.084	0.084	0.085
Total	1.697	1.608	1.817	1.467	1.504	1.468	1.573	1.558	1.591

4.2.2 The effect of initial glucose concentration

It is shown in Figure 5 that the highest substrate loading in feed resulted in a unit production cost of 1,707 $/kg ethanol. Unexpectedly, the lowest unit production cost (1.479 $/kg ethanol) was obtained at the point when moderate glucose concentration was applied. This may due to the difference of ethanol yield (g ethanol/g glucose) under different applied glucose feeding concentrations, as well as the extent of Reaction 1 (or 5 in the Aspen Plus model). With higher glucose feeding concentration (300±6.42 g/L) and the osmotic pressure caused by the very high glucose concentration, yeast cells need longer time and more energy to adapt themselves to the extreme conditions, therefore the ethanol yield, also known as the substrate utilization rate (g ethanol/g glucose), decreased, therefore reduced the profitability of the process. In fact, in all applied experiment conditions with 300±6.42 g/L as the glucose feeding concentration to the fermentor, the residual glucose concentration in the beer remains at 14.39 g/L in average, even after the longest fermentation time (48 hours), this means the substrate in feed was not efficiently utilized, or reflected as a smaller Reaction 1 (or 4) extent. Fermentation with higher glucose loading needs longer fermentation time, and the longer fermentation time may reduce the VHG fermentation efficiency. Moreover, high residual glucose concentration in beer means a small Reaction 1 (or 4) extent as a sign of a waste of unspent glucose, and imposes difficulty of downstream processing, therefore less profitable even though the annual production rate is 5 a little higher (2%) than scenarios with glucose feeding concentration at 250±3.95 g/L. Under the conditions with low glucose feeding concentrations (200±4.99 g/L), despite that glucose can be completely utilized by yeast cells and hence shorter fermentation time was needed, the low glucose feeding concentration still diminishes the efficiency of the entire process, making it not economically preferable.

Usually, VHG fermentation means bio-ethanol fermentation with initial glucose concentration greater than 250 g/L. It was expected that VHG fermentation may reduce the unit production cost due to high ethanol productivity and high ethanol concentration in product, but the simulation results suggested otherwise in the economical aspect.

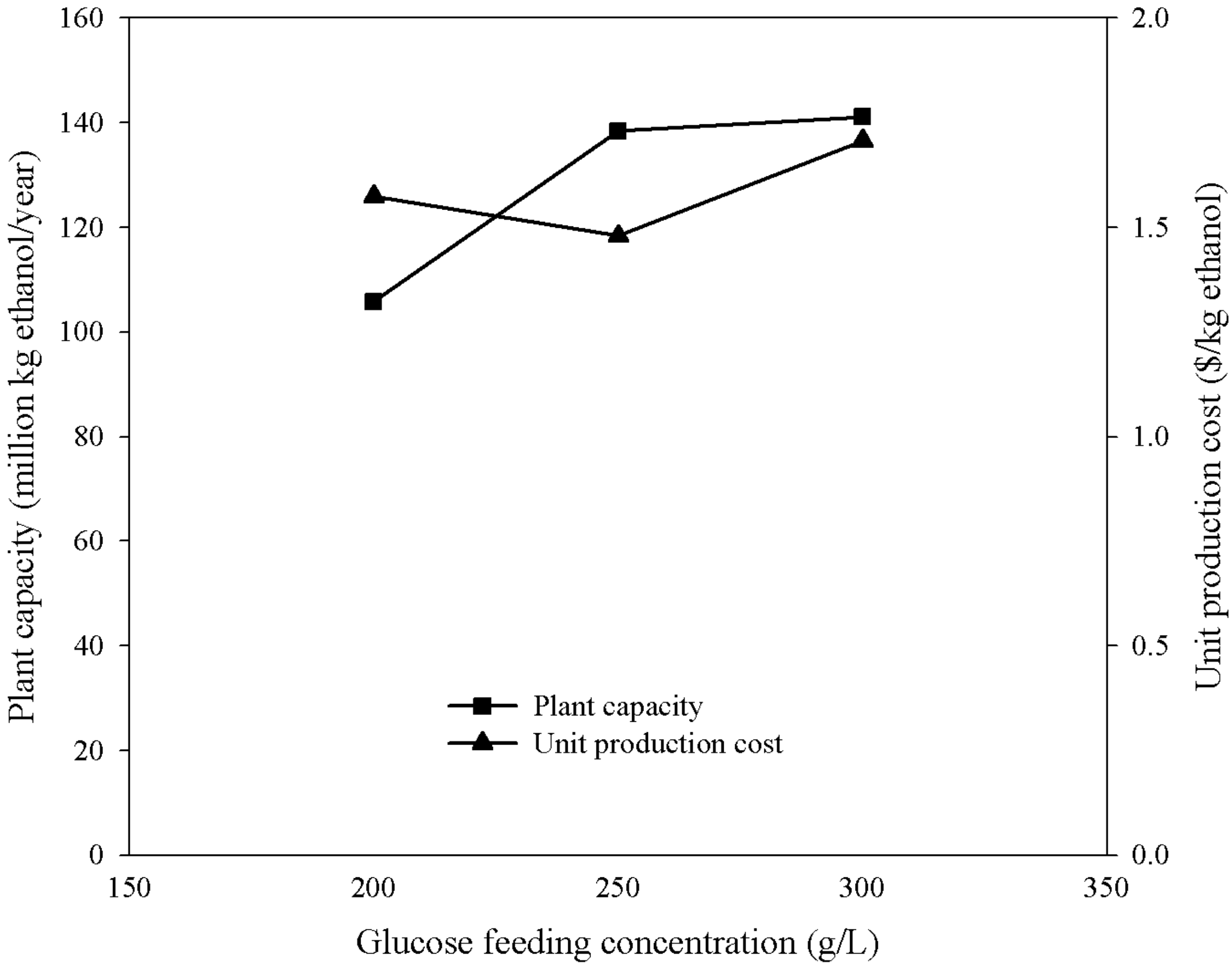

Figure 5 Effects of initial glucose concentration on unit production cost and annual ethanol production rate in Superpro model

Residence time also influences the ethanol yield in fermentor and thus the economical evaluation results. With longer residence time, yeast cells are capable of converting more substrate to product, therefore increase the utilization ratio of substrate. However, there should be an optimum residence time for a certain fermentation process. Longer residence time reduces the efficiency of the entire fermentation process, causing the increase of unit production cost.

4.2.3 The effect of redox potential control

To study the effect of redox potential control on fermentation process and its impact on profitability, two redox potential levels controlled at -100 mV and -150 mV, respectively, were implemented during VHG fermentation and their effects on fermentation were compared to the case of no redox potential control. Results suggested that the redox potential control can stimulate yeast performance and improve fermentation efficiency, thus resulting in higher profit.

At lower glucose feeding concentrations (200±4.99 g/L and 250±3.95 g/L), redox potential control seemed have no significant influence on ethanol yield comparing to the results of high glucose feeding concentration. The effect of redox potential control on ethanol yield shown in Figure 6a is consistent with the conclusion of former observations (Figures 3) that glucose feeding concentration at 250±3.95 g/L results in the highest conversion rate due to the optimal fermentation conditions. The low ethanol yield might be attributed to the osmotic stress resulting from the presence of excess amount of glucose when 300±6.42 g/L glucose was fed to fermentor. Nevertheless, when redox potential was controlled at -100 mV, the ethanol yield decreased significantly by 8.4% from 0.4493 to 0.4114 g ethanol/g glucose. In contrast, when redox potential was controlled at -150 mV, the ethanol yield increased from 0.4114 to 0.4677, even 4.1% greater than that when no redox potential control was applied. From Figure 6a, one can conclude that redox potential control has little to no noticeable effect on ethanol yield at glucose feeding concentration no greater than 250 g/L. However, a remarkable impact on ethanol yield was observed at 300±6.42 g glucose/L. This result is consistent with Lin *et al.* (2010) that under VHG conditions, maintaining redox potential at -150 mV could obtain better ethanol yield. This is to say, redox potential control has significant effects on VHG fermentation process. Controlling redox potential at different levels may result in different ethanol yields. The optimal redox potential level could be further refined for a certain fermentation condition.

It is possible that the effect of redox potential control on VHG fermentation system is reflected by ethanol yield:

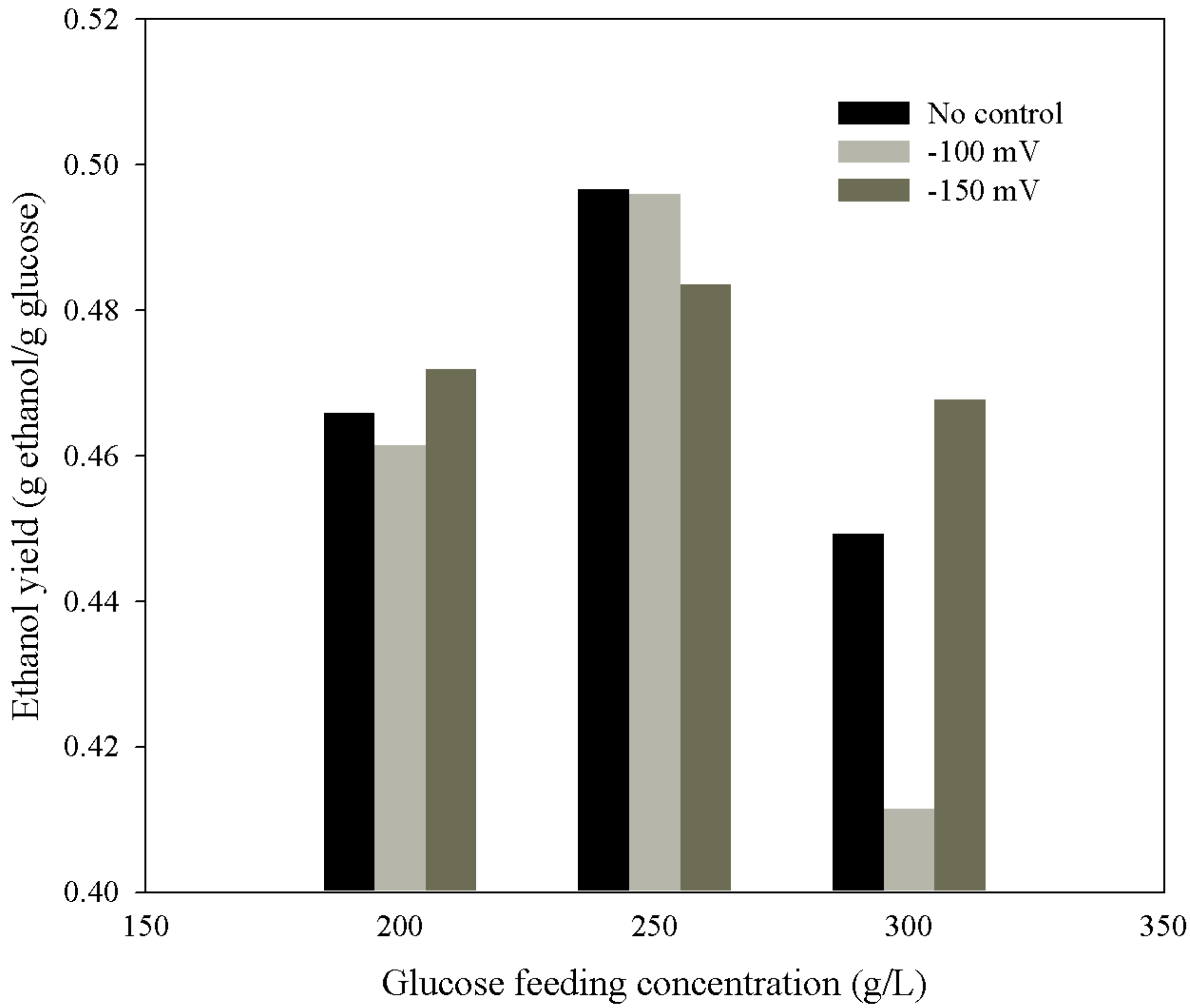

Figure 6a Effects of redox potential control on ethanol yield.

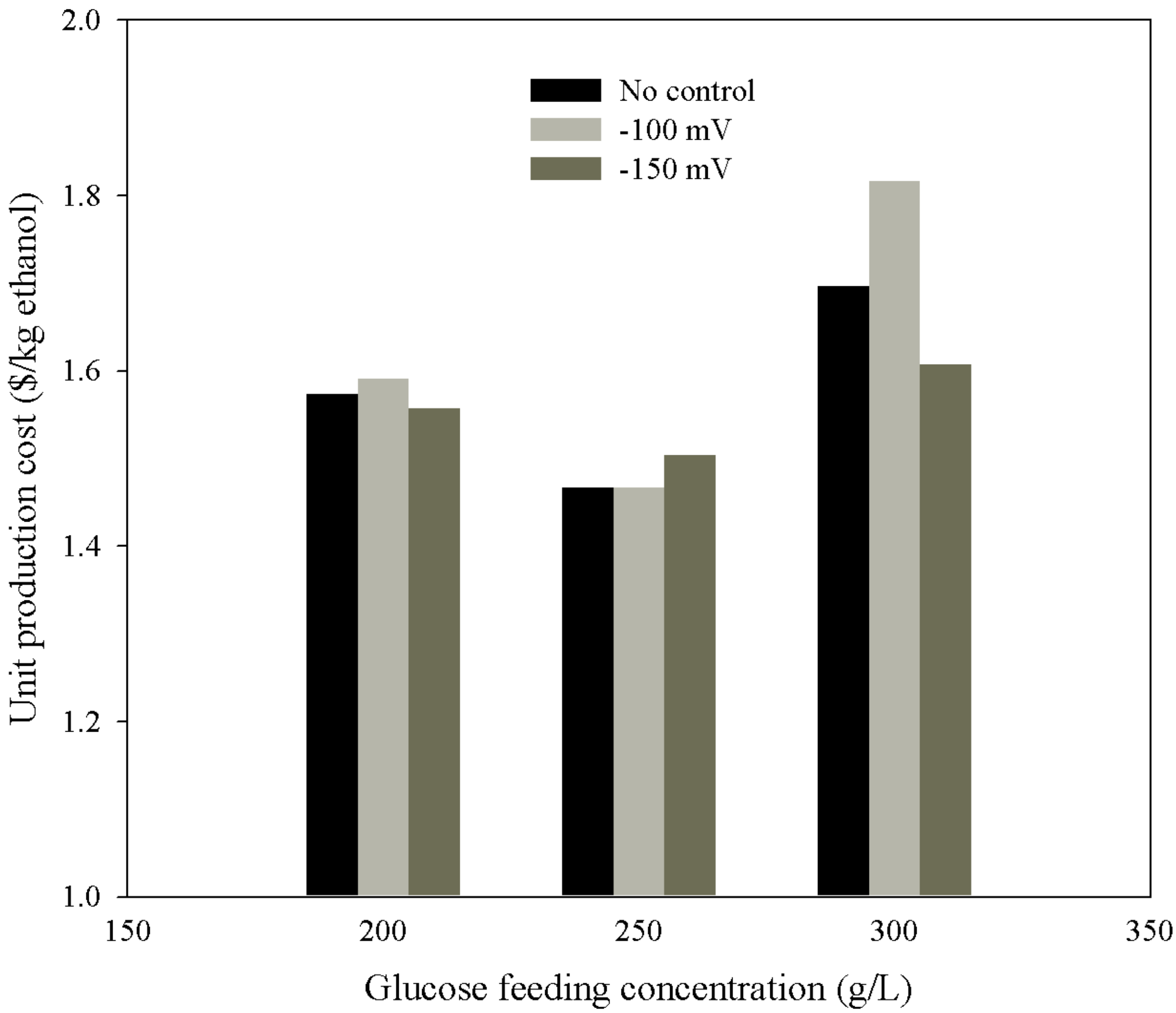

Figure 6b Effects of redox potential control on ethanol unit production cost in Superpro model.

The effects of redox potential and glucose feed on the ethanol unit production cost are shown in Figure 6b. The unit production cost decreased dramatically from 1.817 $/kg to 1.608 $/kg under 300±6.42 g/L glucose feeding concentration when redox potential was controlled from -100 mV to -150 mV. This result is consistent with the result shown in Figure 6a that ethanol yield increases from 0.4114 to 0.4677 under these conditions.

4.3 Process simulation using Aspen Plus 2006

4.3.1 General results

During the process simulation by Aspen Plus, the effects of same glucose feeding concentration (200±4.99, 250±3.95 and 300±6.42 g/L) and same redox potential settings (no control, -150 and -100 mV) were investigated as I did in the Superpro model. The summarized results of economic evaluation are shown in Table 14, the breakdown of unit production cost for each investigated case is listed in Table 15.

Table 14 Results of economic evaluation. Different glucose concentrations in feed stream are denoted as: A = 300±6.42 g/L, B = 250±3.95 g/L, C = 200±4.99 g/L. Different redox potential control levels are denoted as: a = no control, b = -150 mV, c = -100 mV.

	Production rate (10^6 kg ethanol/year)	Unit production cost ($/kg ethanol)	Annual operation cost (10^6 $/year)	Total product sales (10^6 $/year)
Aa	124.65	0.825	102.87	117.97
Ab	131.93	0.780	102.93	119.45
Ac	115.71	0.888	102.79	116.36
Ba	118.98	0.757	90.08	106.40
Bb	115.84	0.777	90.06	106.24
Bc	118.84	0.758	90.08	106.39
Ca	86.54	0.885	76.56	84.42
Cb	87.68	0.873	76.56	84.53
Cc	85.71	0.893	76.56	84.34

Table 15 Breakdown of unit production cost for each case; all values in \$/kg ethanol. Different glucose concentrations in feed stream are denoted as: A = 300±6.42 g/L, B = 250±3.95 g/L, C = 200±4.99 g/L. Different redox potential control levels are denoted as: a = no control, b = -150 mV, c = -100 mV.

Cost item (\$/kg Ethanol)	Aa	Ab	Ac	Ba	Bb	Bc	Ca	Cb	Cc
Raw material cost	0.738	0.698	0.795	0.676	0.694	0.676	0.788	0.777	0.795
Utilities cost	0.012	0.012	0.012	0.011	0.011	0.011	0.012	0.012	0.012
Operating Labor Cost	0.007	0.007	0.008	0.008	0.008	0.008	0.011	0.010	0.011
Maintenance Cost	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.001
Operating Charges	0.002	0.002	0.002	0.002	0.002	0.002	0.003	0.003	0.003
Plant Overhead	0.004	0.004	0.004	0.004	0.004	0.004	0.006	0.006	0.006
G and A Cost	0.061	0.058	0.066	0.056	0.058	0.056	0.066	0.065	0.066
Total	0.825	0.780	0.888	0.757	0.777	0.758	0.885	0.873	0.893

4.3.2 Sales analysis

The sales analysis results of all studied scenarios with different glucose feeding concentrations and different redox potential settings are listed in Table 16. Ethanol is the main product of the process, while DDGS and CO_2 are byproducts, selling prices of which are presented in Table 1.

Table 16 Sales analysis for each applied condition; Different glucose concentrations in feed stream are denoted as: A = 300±6.42 g/L, B = 250±3.95 g/L, C = 200±4.99 g/L. Different redox potential control levels are denoted as: a = no control, b = -150 mV, c = -100 mV.

	Total operating cost (million $/year)	Total product sales (million $/year)	Payout period (years)
Aa	102.87	117.97	6.08
Ab	102.93	119.45	5.71
Ac	102.79	116.36	6.59
Ba	90.08	106.40	5.32
Bb	90.06	106.24	5.35
Bc	90.08	106.39	5.32
Ca	76.56	84.42	8.47
Cb	76.56	84.53	8.39
Cc	76.56	84.34	8.52

Payout Period is the expected number of years required to recover the original investment in the project. This parameter indicates the length of time that the facility needs to operate in order to recover the initial capital investment (total capital cost plus working capital). The results shown in Figure 7 suggested that for an ethanol plant with a capacity of 85~130 million kg ethanol/year, maintaining the glucose feeding concentration to the fermentor at around 250 g/L resulted in the shortest payout period of 5.33 years in average, with or without redox potential control. If 300±6.42 g/L glucose feeding concentration to the fermentor is applied, it is essential to have the redox potential only controlled at -150 mV in the fermentor to limit the process payout period within 6 years. In addition, fermentation processes with glucose feeding concentration at around 200 g/L to the fermentor were estimated to have payout period of over 8 years under all evaluated scenarios. This makes the process much less profitable comparing to scenarios with higher glucose feeding concentrations.

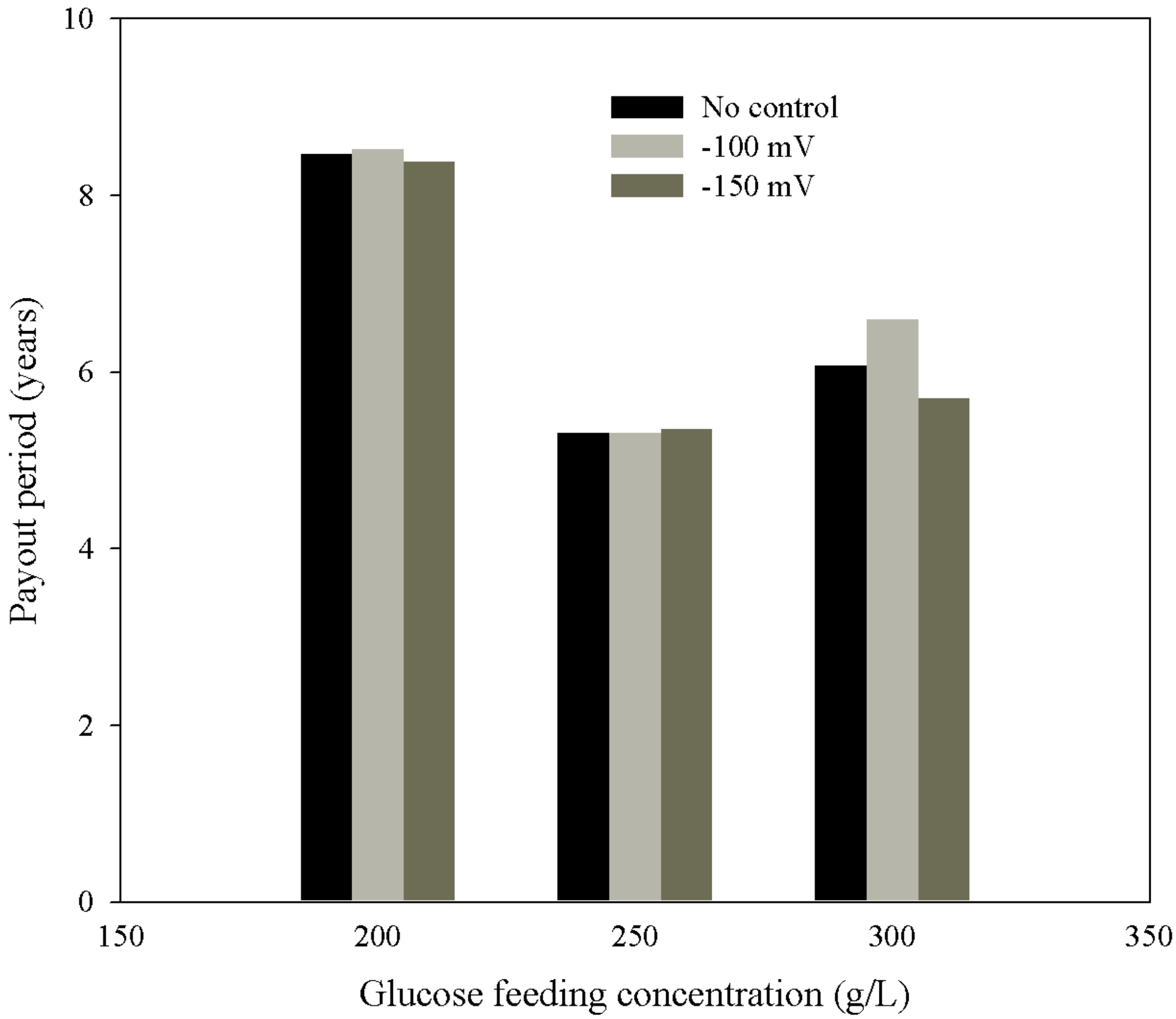

Figure 7 Sales analysis of payout period on different glucose feeding concentrations and redox potential controls in Aspen Plus model.

4.3.3 Effect of glucose feeding concentration

Results with similar trends were obtained from the Aspen Plus model, as shown in Figure 8, the highest glucose loading in feed did not result in the lowest unit production cost, and the lowest unit production cost (0.764 $/kg ethanol) was obtained when the glucose feeding concentration at 250±3.95 g/L was applied. Besides the difference of actual unit production cost values, Production rate of scenarios with glucose feeding concentration at 300±6.42 g/L is 5% higher than scenarios with glucose feeding concentration at 250±3.95 g/L.

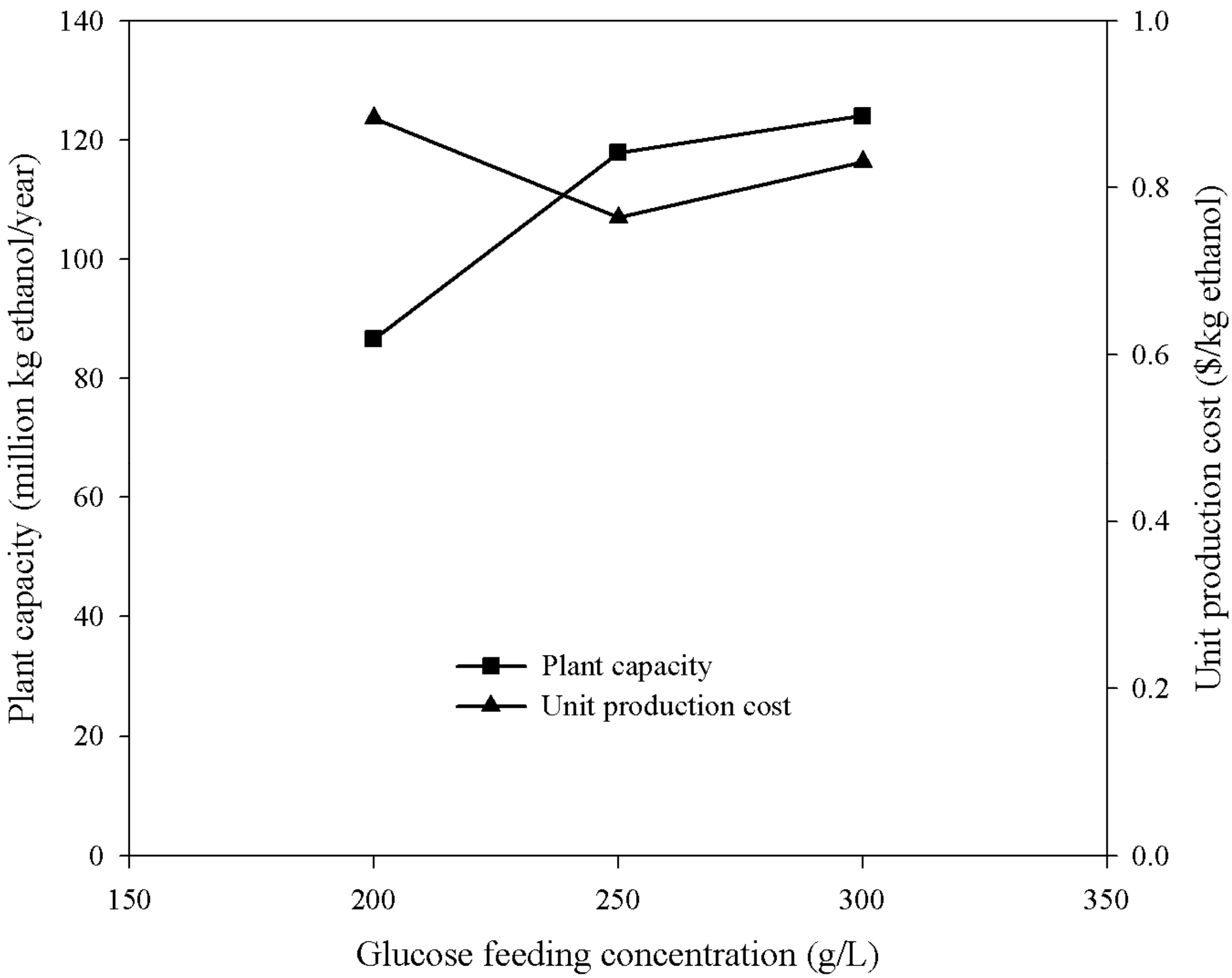

Figure 8 Effect of glucose feeding concentration on Production rate and unit production cost in Aspen model.

The selling price of the DDGS stream was calculated based on its moisture content and the dry

DDGS price, which was presented in Table 1. In addition, higher glucose feeding concentration results in higher biomass content thus less moisture in DDGS as a byproduct stream, therefore higher selling price for DDGS as another revenue stream, but still not significant to make the whole process more profitable than the scenarios with moderate glucose feeding concentration (250±3.95 g/L).

The influence of glucose feeding concentration on ethanol yield along with unit production cost is shown in Figure 9, values used in the figure were averages of all investigated conditions under one certain glucose feeding concentration, difference of redox potential control effects were not considered here. The lowest unit production cost (0.764 $/kg ethanol) and highest ethanol yield (0.4920 g ethanol/g glucose) were achieved when the moderate glucose feeding concentration (250±3.95 g/L) were applied. In contrast, high glucose feeding concentration (300±6.42 g/L) led to the lowest ethanol yield (0.4428 g ethanol/g glucose in average), and low glucose feeding concentration (200±4.99 g/L) resulted in the highest unit production cost (0.884 $/kg ethanol in average), both of which are not economically preferable. This result suggests that under moderate glucose feeding concentration, the fermentation system neither produces biomass more than it needs, nor waste glucose from the feed.

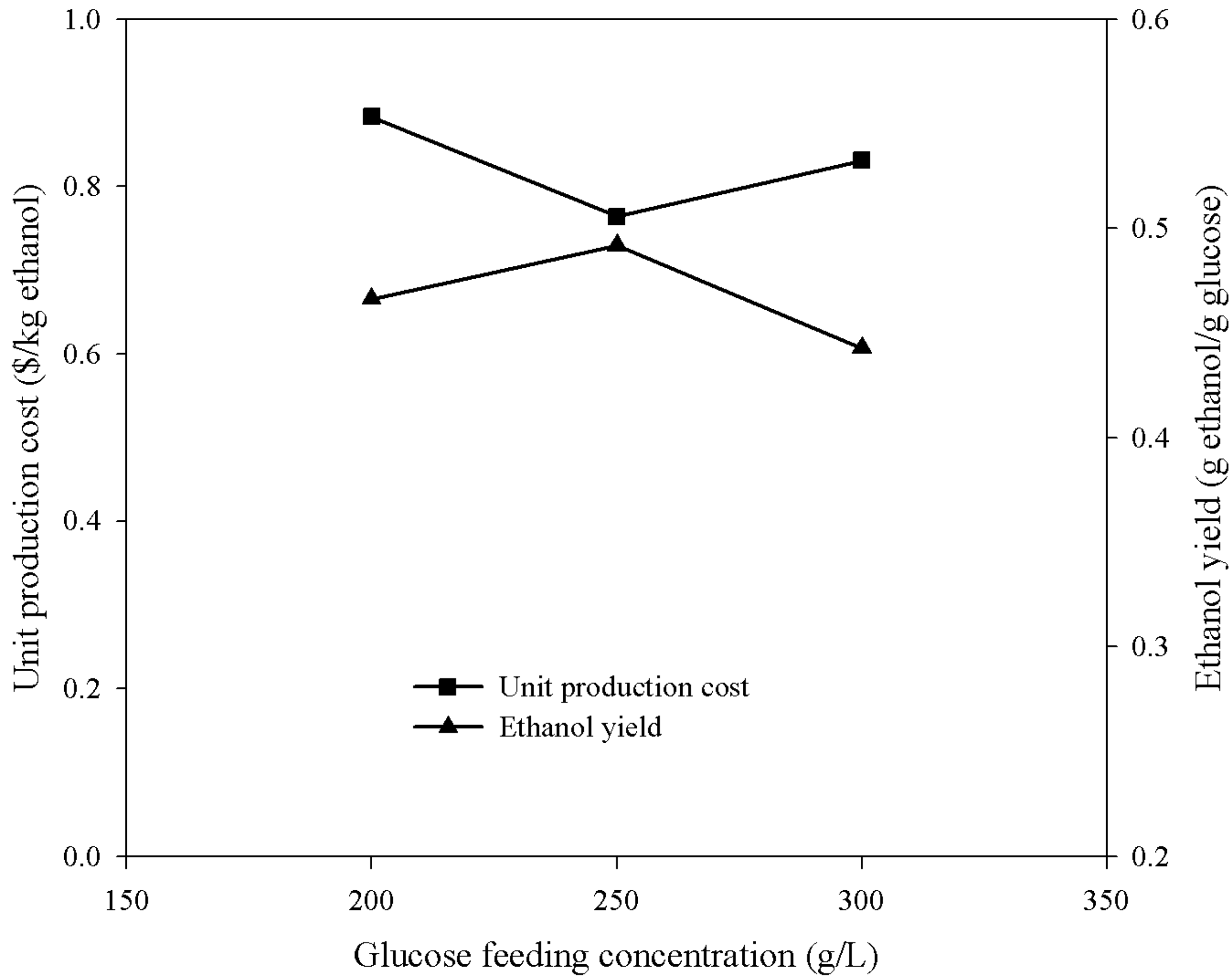

Figure 9 Effect of glucose feeding concentration on unit production cost and ethanol yield in Aspen model.

4.3.4 Effect of redox potential control

To study the effect of redox potential control on fermentation process and its impact on the profitability, two redox potential levels controlled at -100 mV and -150 mV, respectively, were implemented during VHG fermentation and compared to the scenarios without redox potential control. Results suggested that redox potential control can enhance yeast performance and improve fermentation efficiency, thus resulting in higher profit.

Effects of redox potential and glucose feeding concentration on the ethanol unit production cost are shown in Figure 10. Under 300±6.42 g /L glucose feeding concentration, the unit production cost of ethanol increased from 0.825 \$/kg when no redox potential control was applied, to 0.888 \$/kg when -100 mV redox potential was applied, and decreased dramatically to 0.780 \$/kg when redox potential was reduced from -100 mV to -150 mV. This result is also consistent with the result shown in Figure 6a that ethanol yield increases from 0.4114 to 0.4677 when redox potential was reduced from -100 mV to -150 mV. Applying an optimal redox potential control level to the fermentation process may not only increase the ethanol yield in the fermenter thus reduce the unit production cost, but also avoid procedural waste of raw material when VHG fermentation process is applied for higher productivity and profitability.

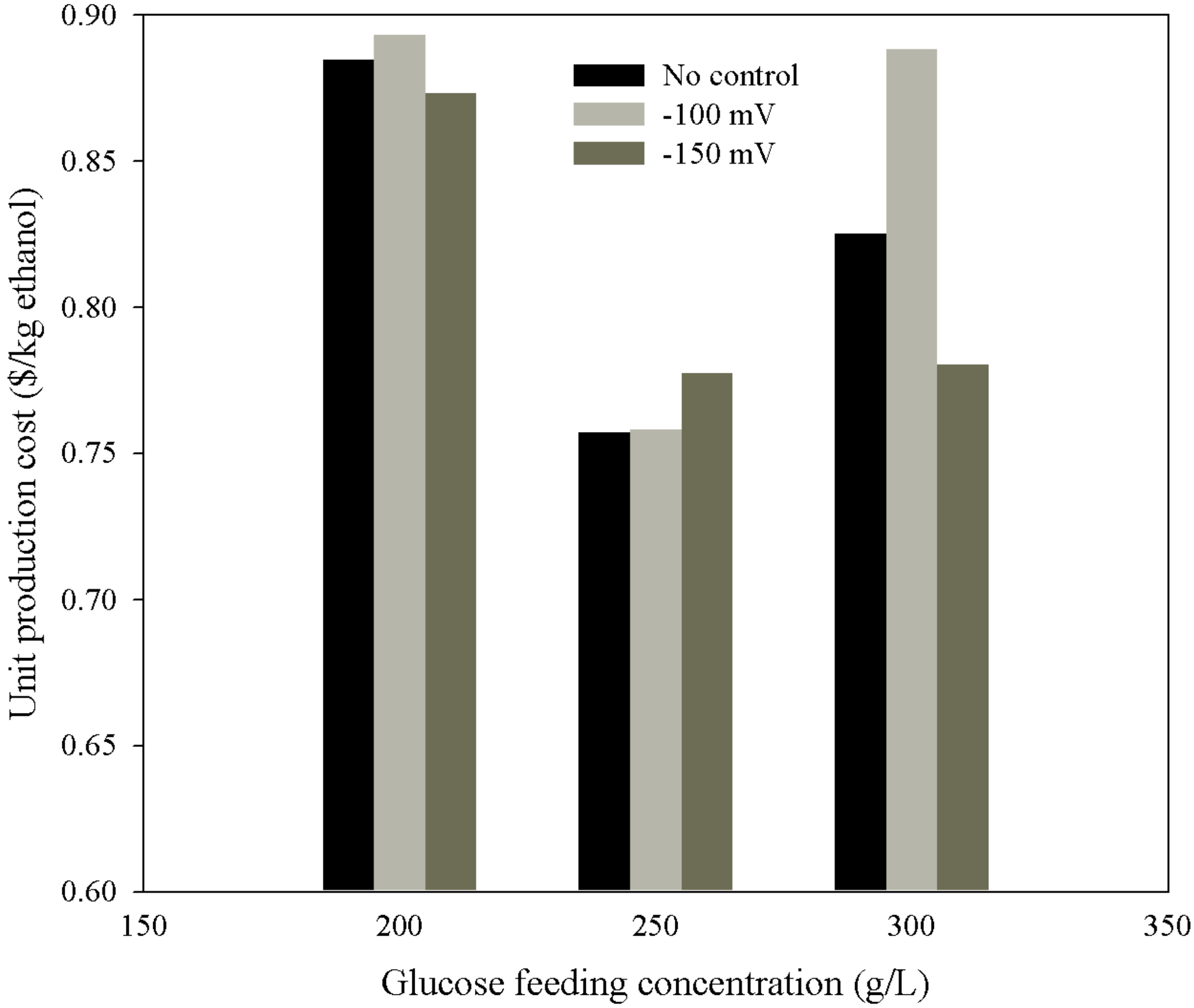

Figure 10 Effect of redox potential control on ethanol unit production cost in Aspen model.

4.4 Comparison of Superpro and Aspen Plus models

4.4.1 Model basis

Brief illustrations of the Superpro model and Aspen Plus model were compared in Figure 11. As mentioned before, because the software Superpro Designer used in the first process modeling has a disadvantage that the number of equipment units is limited to be less than 25 in one process model, therefore the liquefaction and saccharification sections of an ethanol producing were ignored, as well as the treatment procedures of primary DDGS stream (centrifugation, evaporation and drying).

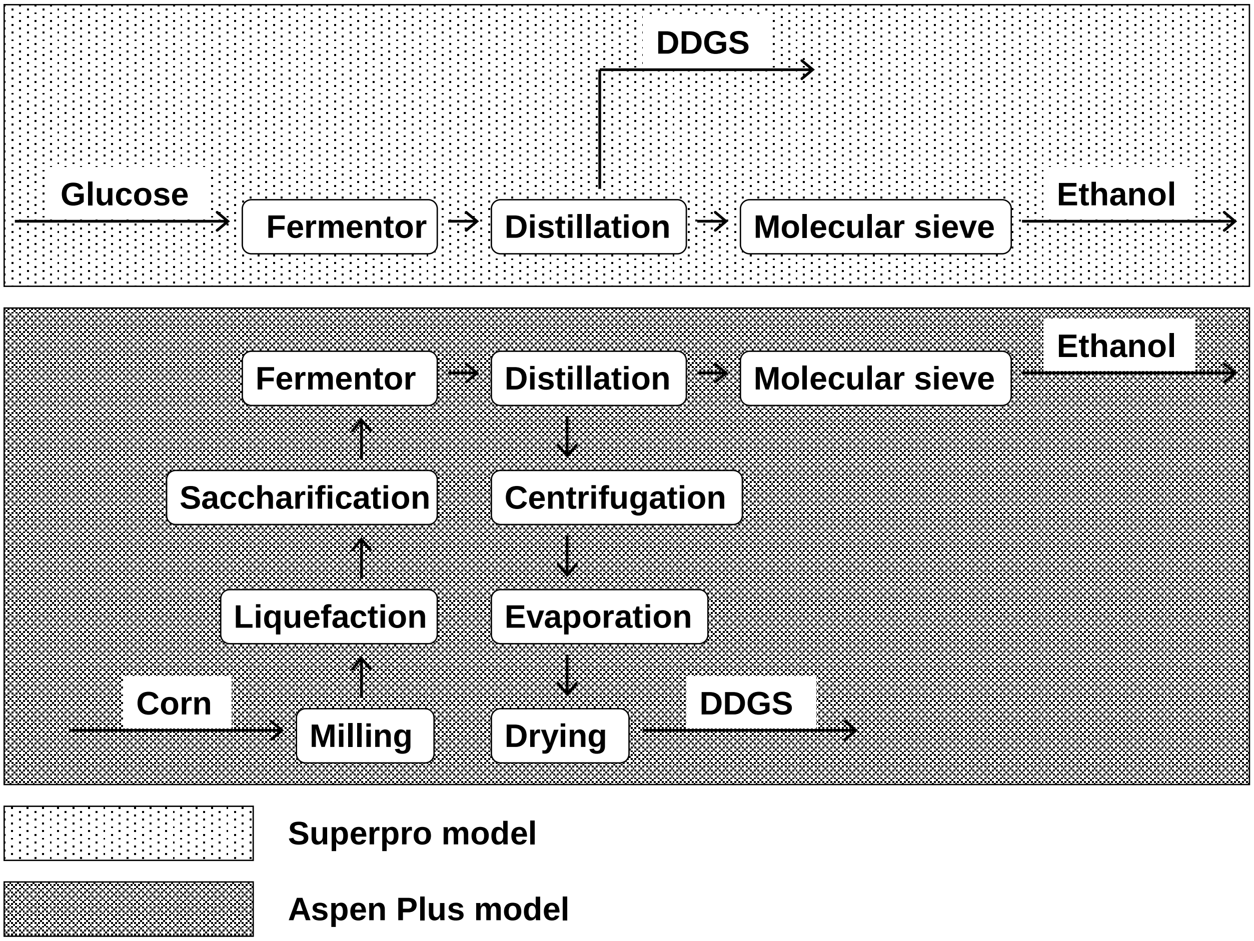

Figure 11 Brief illustrations of the two models used for process simulation.

In the Superpro model, in order to approximate the product composition of the saccharification section, glucose solution in certain concentrations with certain ingredients (protein, oil, non-fermentable solids, non-starch polysaccharides), was directly used as the raw material feed to the fermentor. On the other hand in the Aspen Plus model, corn (composed of starch, protein, oil, non-starch polysaccharides, non-fermentable solids) was used as the raw material feed into the whole process. Different feed stocks of the two models will predictably achieve different results of economic evaluation, this will be discussed in section 4.4.3 “Model sensitivity to feed stocks”.

In laboratory fermentation experiments, different redox potential controls were applied under different initial glucose concentrations. However, in both of the two process simulators, concentration of a certain component in the feed stream can not be simply defined as an input parameter. In this occasion, mass composition of a certain component was used to precisely manipulate the glucose concentration in feed of the fermentor. In general, mass composition of glucose in the feed stream to fermentor was varied to achieve designed glucose concentration in the very stream, while starch content in the feed stream to the milling procedure of the Aspen Plus model was varied to achieve designed glucose concentration in the feed stream to fermentor.

In addition, because of the number limitation of equipment units used in the Superpro model, many recycle streams used in a real ethanol plant to save raw materials and energy was also ignored. Therefore, Aspen Plus was used to build a new model of an ethanol plant to overcome the disadvantages of the Superpro model mentioned above, and another software Aspen Icarus Process Evaluator was used for economical evaluation.

4.4.2 Equipment units

Equipment units used in two models are listed in Table 17. For the purpose of better understanding of block type in the Aspen model, detailed description were presented in Table 18. As shown in Figure 11, the Aspen Plus model is much more complicated hence a more accurate model than the Superpro model to simulate the production process of a real ethanol fermentation plant.

Table 17 Unit blocks used in both models.

Superpro model (17 blocks)		Aspen Plus model (37 blocks)	
Block Name	Block Type	Block Name	Block Type
PM-101	Centrifugal Pump	AGETANK	Flash2
C-101	Distillation Column	BEERCOL	RadFrac
PM-102	Centrifugal Pump	CENTRIF	SSplit
HX-103	Heat Exchanger	CONDENSE	Flash2
PM-103	Centrifugal Pump	CTFSSPLT	FSplit
MX-102	Mixer	DDGSDRYR	Flash2
C-102	Distillation Column	DEGAS	Flash2
CSP-101	Component Splitter	EVAP	Flash2
PM-104	Centrifugal Pump	FERMENT	Rstoic
PM-105	Centrifugal Pump	H2OMIXER	Mixer
C-103	Distillation Column	HEAT1	Heater
V-103	Flat Bottom Tank	HEAT2C	Heater
V-101	Fermentor	HEAT2H	Heater
V-104	Blending Tank	HEAT3	Heater
GP-101	Gear Pump	HEAT4C	Heater
AF-101	Air Filter	HEAT4H	Heater
C-104	Absorber	HEAT5	Heater
		HEAT6H	Heater
		HEAT7C	Heater
		HEAT7H	Heater
		HEAT8	Heater
		HEAT9C	Heater
		HEAT9H	Heater
		HEAT10	Heater
		HEAT11	Heater
		HEAT12	Heater
		LIQUEFY	Heater
		MILL	Sep
		MIXCTF	Mixer
		MIXDDGS	Mixer
		MOLSIEVE	Sep
		PCSPLIT	FSplit
		PRESS	Pump
		RECTIFY	RadFrac
		SACCHAR	Rstoic
		SCRUBBER	RadFrac
		SEPETOH	Sep

Table 18 Description of unit type in Aspen Plus model.

Block type	Category	Description
Flash2	Separators	Two-outlet flash
RadFrac	Columns	Rigorous 2 or 3-phase fractionation
SSplit	Mixers/Splitters	Substream splitter
FSplit	Mixers/Splitters	Stream splitter
Rstoic	Reactors	Stoichiometric reactor based on known fractional conversions of extents of reactions
Mixer	Mixers/Splitters	Stream mixer
Heater	Heat Exchangers	Thermal and phase state changer
Sep	Separators	Component separator
Pump	Pressure Changers	Pump or hydraulic turbine

4.4.3 Model sensitivity to feed stocks

The influence of different feed stocks on unit production cost is shown in Table 19. The unit production cost estimated by Superpro model is roughly twice of Aspen Plus's estimated value due to the great difference of feed stock purchasing price. However, even a huge gap exists between the actual estimated values of the two models, a similar trend of these results was still observed, as shown in Figure 12.

Table 19 The influence of different feed stocks on unit production cost. Different glucose concentrations in feed stream are denoted as: A = 300±6.42 g/L, B = 250±3.95 g/L, C = 200±4.99 g/L.

	Superpro model	Aspen Plus model
Feed stock	Glucose (Dextrose)	Corn
Purchasing price ($/kg)	0.6360	0.2482
Unit production cost ($/kg ethanol)		
A	1.7070	0.8313
B	1.4793	0.7642
C	1.5737	0.8837

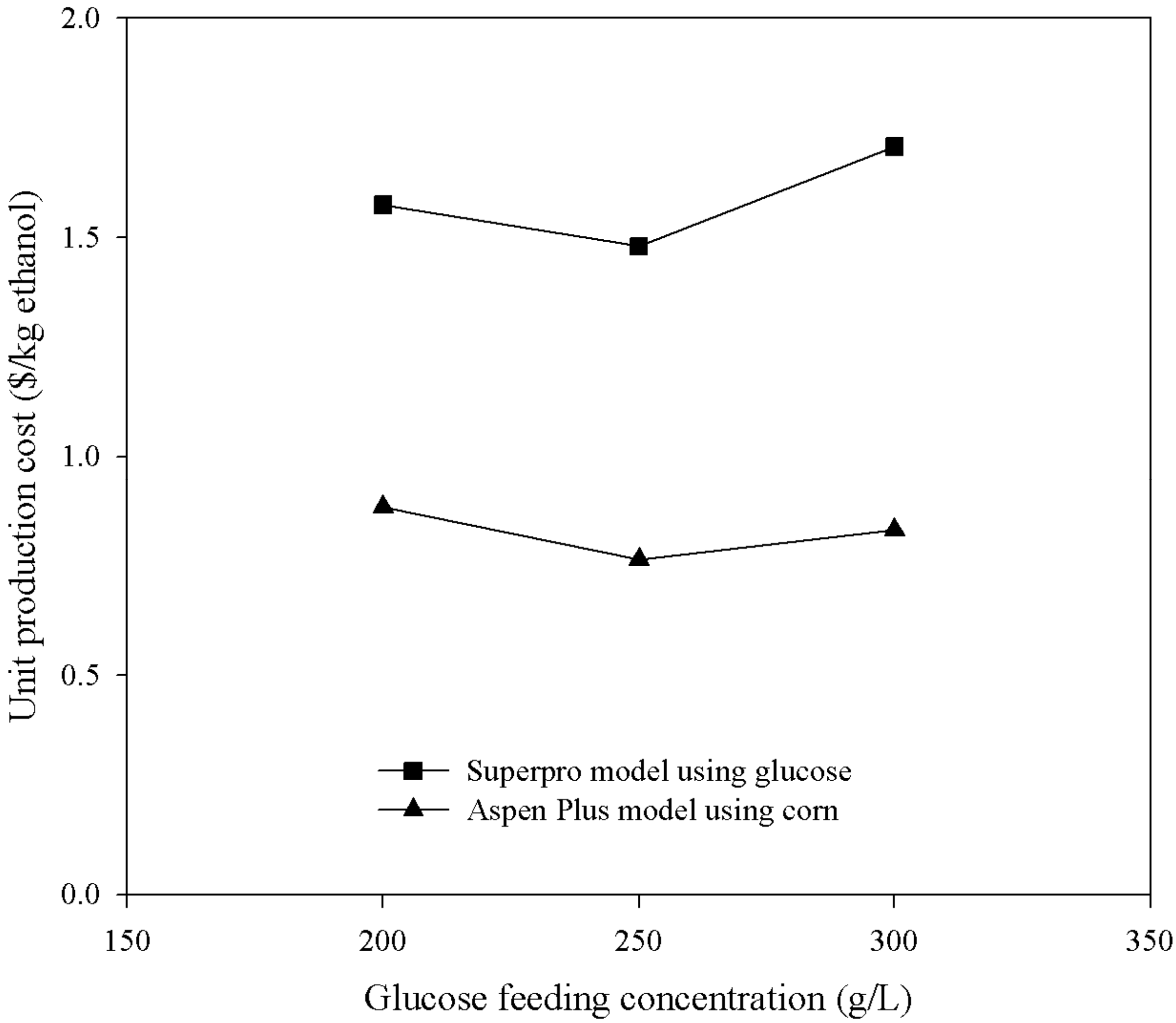

Figure 12 Effect of different feed stocks used by different models on unit production cost.

As shown in Figure 12, the lowest unit production cost was achieved under 250±3.95 g/L feeding glucose to fermentor, due to the highest ethanol yield (g ethanol/g glucose) under this condition. Nevertheless, in the Superpro model, unit production cost estimated under 200±4.99 g/L glucose feeding concentration is lower than the value under 300±6.42 g/L feeding glucose; while in the Aspen Plus model this order went to the opposite way. This result might be caused by the sensitivity difference of the two models to raw material cost, which accounts for roughly 90% of the total unit production cost of ethanol, as shown in Table 20.

Table 20 Percentage of raw material cost in total unit production cost of two models. Different glucose concentrations in feed stream are denoted as: A = 300±6.42 g/L, B = 250±3.95 g/L, C = 200±4.99 g/L. Different redox potential control levels are denoted as: a = no control, b = -150 mV, c = -100 mV.

		Superpro model			Aspen Plus model		
		Scenario percentage	Condition average	Model average	Scenario percentage	Condition average	Model average
A	a	91.10%	91.09%	89.92%	89.47%	89.48%	89.24%
	b	90.92%			89.41%		
	c	91.25%			89.54%		
B	a	89.64%	89.77%		89.22%	89.23%	
	b	89.89%			89.24%		
	c	89.78%			89.22%		
C	a	88.94%	88.91%		89.02%	89.02%	
	b	88.86%			89.01%		
	c	88.93%			89.02%		

It can be seen in Table 20 that even the percentages of raw material cost in total unit production cost of two models are quite close, but variations of the condition averages which represent the average value under different glucose feeding condition in the two models are relatively large. Since the Superpro model has only 17 equipment units compared to 37 equipment units in the

Aspen Plus model as listed in Table 17, raw material cost will account for more share in the total unit production cost. As a result, the Superpro model is more sensitive to variations of raw material feed, especially when the feed is very high under VHG conditions. In addition, as discussed above that low glucose feeding concentration (200±4.99 g/L) diminishes the efficiency of the entire process, this diminishing effect is more considerable in the more complicated Aspen Plus model than in the relatively simple Superpro model. Therefore, the highest unit production cost was obtained under 300±6.42 g/L feeding glucose in the Superpro model, and under 200±4.99 g/L feeding glucose in the Aspen Plus model.

4.4.4 Product streams

Main properties of product streams (product purity) of the two models are compared in Table 21. Due to the use of molecular sieves, purity of ethanol in the final product streams of both models is quite close at over 99% of total mass.

Table 21 Comparison of product streams in the two models. Different glucose concentrations in feed stream are denoted as: A = 300±6.42 g/L, B = 250±3.95 g/L, C = 200±4.99 g/L.

Product streams	Superpro model			Aspen Plus model		
	A	B	C	A	B	C
Main product						
Ethanol (mass purity)	99.71%	99.68%	99.56%	99.34%	99.30%	99.37%
Byproduct						
DDGS (moisture content)	80.76%	86.79%	86.72%	31.65%	27.60%	28.82%
CO_2 (mass purity)	74.46%	78.12%	79.09%	99.29%	99.31%	99.35%

On the other hand, the quality of byproduct streams is quite different from each other. According to data from Agricultural Marketing Resource Center of ERS/USDA, 65~ 70% moisture in DDGS stream (or called as Wet Distillers Grain) is allowed for the yield stream to be directly sold as byproduct. Moisture content in the stream is usually controlled at 50~55% for Modified Wet Distillers Grain, and 10% for Dried Distillers Grain. For this concern, DDGS yield from the Superpro model needs further dehydration to be sold on market, while DDGS stream yield form the Aspen Plus model can be directly sold on market as byproduct of ethanol fermentation process.

For the CO_2 stream produced from the Aspen Plus model, essentially all gas emission is CO_2 and no further processing is needed to recover CO_2. But for the Superpro model, mass purity of CO_2 produced from the process is not high enough for the stream to be directly sold as byproduct, further treatment is still needed to remove nitrogen and oxygen in the stream.

4.4.5 Reaction accuracy

It should be noticed that even though the main reaction in the fermentor of both models (Reaction 1 in the Superpro model and Reaction 5 in the Aspen Plus model) is almost the same, and the same coefficients α, β are varied to apply laboratory fermentation results to both models, the accuracy of these two coefficients in the two models is different. The coefficients in the Aspen Plus model can be accurate to the fourth decimal place or more, while only second decimal place accuracy is allowed in the Superpro model.

In Reaction 1 in the Superpro model (or Reaction 5 in the Aspen Plus model), the theoretical value of α is 2, and thus 0 for β. However, under real fermentation conditions, certain amount of biomass is produced from the substrate during fermentation, therefore α is always smaller than 2 in real conditions. Among all laboratory fermentation experiments, α is determined to range from 1.5775 to 1.9884 depending on glucose feeding concentrations and redox potential setting applied to the fermentor.

For instance, in one fermentation experiments of which α is determined to be 1.7944, Reaction 4 in the Aspen Plus model will be defined as:

$$\text{Glucose} \rightarrow 1.7944\ \text{CO}_2 + 1.7944\ \text{Ethanol} + 0.1234\ \text{YDM}$$

While Reaction 1 in the Superpro model can only be defined to be (β is dependent to α to ensure mass balance of the equation, YDM in the Aspen model and Yeast Dry Matter in the Superpro model are defined with different molecular weights):

$$\text{Glucose} \rightarrow 1.79\ \text{Carbon Dioxide} + 1.79\ \text{Ethyl Alcohol} + 1.05\ \text{Yeast Dry Matter}$$

In this way, even exactly the same fermentation conditions were applied, the simulated ethanol yield of the Superpro model is actually 2.45‰ lower than that of the Aspen Plus model. For a plant with a capacity of 100 million kg ethanol/year, simply decrease in ethanol yield by 2.45‰ means reduction in Production rate by 245,000 kg ethanol/year, or loss of nearly 0.18 million \$/year in main product sales.

Under large scale productions, even the smallest variations of the reactions defined in the fermentor may eventually cause huge difference of the final evaluation results. The Aspen Plus model obviously achieves better accuracy on process simulation than the Superpro model.

4.5 Disposal of CO_2 produced during fermentation

During the fermentation process which yeast cells convert glucose to ethanol, equal number of carbon dioxide molecules will be produced. For a plant with a capacity of 100 million kg/year of ethanol, 95.53 million kg/year of carbon dioxide will also be produced. Three options for the disposal of CO_2 were presented in Figure 13.

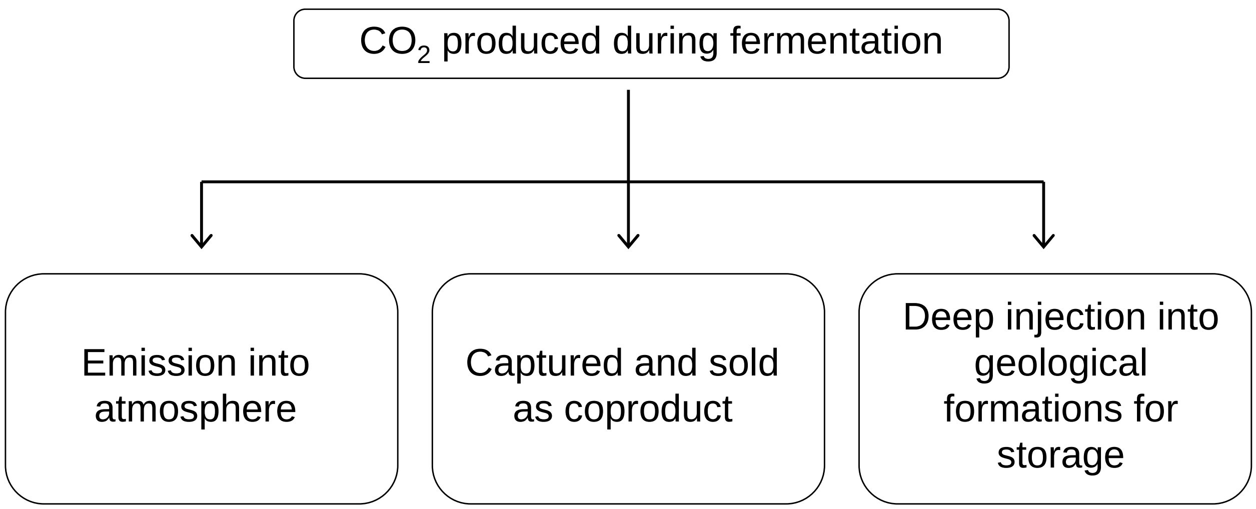

Figure 13 Options for disposal of CO_2 during bio-ethanol fermentation.

Most fermentation facilities emit their CO_2 to the atmosphere. This is not only a waste of resource, but more importantly not environmental preferable since CO_2 is one of the major greenhouse gases that causing global warming problem. In some facilities, CO_2 is assumed to be sold for carbonate beverages or dry ice production. Selling CO_2 as a byproduct of fermentation process has no significant impact on reducing the production cost of ethanol (Wingren *et al.*, 2003), but is still profitable for facilities with large CO_2 production rate, and is environmental friendly.

For a fermentation process like the studied one, essentially all gas emissions is CO_2 and no further processing is needed to recover CO_2 (Möllersten and Moreira, 2003). The selling price of industrial level CO_2 is estimated to be 15.94 \$/ton (Wingren *et al.*, 2003), then for the process with a capacity of 100 million kg ethanol/year, selling CO_2 as a byproduct will bring in 1.52 million \$/year as extra income. Selling CO_2 as a byproduct is profitable, however, it is still questionable whether this could be actually implemented if many ethanol plants were established, because the market for CO_2 could become saturated to consume such large amount of CO_2.

In fact, there are growing commercial-scale experiences that CO_2 is injected into deep underground geological formations to avoid leakage into atmosphere (Bachu *et al.*, 2003). The experience of acid-gas injection operations showed that CO_2 sequestration in geological media is a mature and safe technology that can successfully be expanded to and applied in large-scale operations that will reduce CO_2 emissions into the atmosphere from large CO_2 point sources (Kheshgi and Prince, 2005). For the scenario mentioned above, the CO_2 production rate is assumed to be 95.53 million kg/year, and the plant locates 500 km away from the deep injection site, therefore the capture cost is estimated to be 50 \$/ton CO_2 including capture and transportation (Möllersten and Moreira, 2003), so the CO_2 deep injection cost for the plant will be 4.78 million \$/year. Shorter transportation distance and larger Production rate further reduces the unit cost of CO_2 storage and transportation, evaluation parameters can be obtained from

McCoy (2008) and (Möllersten and Moreira, 2003) for different scenarios.

Furthermore, if fermentation CO_2 can be stored (e.g. in a geological reservoir), some of the CO_2 taken up during crop growth would not be released back to the atmosphere but sequestered underground. If this exceeded the fossil carbon emitted during ethanol production, then the production of ethanol would result in the net removal of CO_2 from the atmosphere. Note the deep injection operations for carbon sequestration are also applicable to many other sites around the world (Thambimuthu, 2004).

The compression and transport of CO_2 to the sequestration site would add cost (Kheshgi and Prince, 2005). McCoy (2008) gave some methods to estimate the pipeline cost for large amount CO_2 transportation based on different flow rates and distances. However, in North America, such acid-gas deep injection operations were already started since 1989 (Bachu *et al.*, 2003). Using existed pipelines to transport CO_2 to sequestration sites or building CO_2 generating sources such bio-ethanol fermentation plants near deep injection sites will lower the cost of deep injection.

CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

In this study, Superpro Designer as one of the process simulators was mainly used to explore the effects of applied glucose feeding concentrations and redox potential control settings on process economics, since the Superpro model is not a complete process for ethanol fermentation, results of economical evaluation were only used to compare to each other to study effects of different applied conditions on fermentation, thus not appropriate for reference on market. On the other hand, results from Aspen utilities (Aspen Plus as the simulator, Aspen IPE as the evaluator) are quotable to be compared with real market prices.

According to simulated results, VHG condition of 300±6.42 g/L glucose feeding concentration did not achieve the expected reduction on unit production rate of ethanol. The results suggested that the most profitable glucose feeding concentration to the fermenter is around 250±3.95 g/L among all studied scenarios, which gives the lowest ethanol unit production cost and shortest process payout period, with or without redox potential control. Application of VHG fermentation process requires not only an industrial yeast strain to efficiently utilize fermentable substrates within shorter residence time, but also approaches to reuse residual saccharides in the output stream of the fermentor.

Redox potential control has certain effects on fermentation process, especially for VHG fermentation process. Results suggest that controlling redox potential level at -150 mV during fermentation increases the ethanol yield, therefore considerably reduces the unit production cost under VHG conditions. However, the optimal combination of redox potential control level and glucose feeding concentration requires further examination.

Since large amount of CO_2 is produced during fermentation process, to capture and sell CO_2 is profitable for plants with large capacity despite the extra costs of a CO_2 recovery system. In addition, CO_2 is known as the major greenhouse gas which causes global warming. Despite that the deep injection alternative for disposal of CO_2 produced during fermentation is not economically preferable comparing to whether emitting CO_2 to atmosphere or selling it as a byproduct, the deep injection operation to reduce CO_2 emission to atmosphere is currently much more environmental friendly, and is of great long term benefits.

5.2 Recommendations

As discussed above, redox potential setting has different effects on ethanol yield (substrate utilization rate) according to different initial glucose concentrations of fermentation. In laboratory experiments, only two redox potential settings, -100 mV and -150 mV, were compared to no redox potential control conditions to study its effect on fermentation process. In future studies, more redox potential setting levels might need to be applied to determine the optimum value for the highest ethanol yield. Besides, these redox potential controlled fermentation experiments were carried out in lab scale, therefore further and more specific tests are required for industrial scale fermentation.

REFERENCES

Bachu, S., J. J. Adams, K. Michael, and B. E. Buschkuehle, "Acid gas injection in the Alberta Basin: a commercial-scale analogue for CO_2 geological sequestration in sedimentary basins," Second annual conference on carbon sequestration, Washington.D.C, National Energy Technology Laboratory, United States Department of Energy (2003).

Casey, G.P., C.A. Magnus, and W.M. Ingledew, "High-Gravity Brewing: Effects of Nutrition on Yeast Composition, Fermentative Ability, and Alcohol Production," *Applied and Environmental Microbiology*, 639 (1984).

Duncan, M., "U. S. Federal Initiatives to Support Biomass Research and Development," *Journal of Industrial Ecology*, **7**(3-4), 193(2003).

Eidman, V.R., "Renewable Liquid Fuels: Current Situation and Prospects," *Choices* **21**(1), 15(2006).

EthanolIndia, http://www.ethanolindia.net/molecular_sieves.html, August 1, 2011.

Gibreel A., J.R. Sandercock, J. Lan, L.A. Goonewardene, R.T. Zijlstra, J.M. Curtis, and D.C. Bressler, "Fermentation of barley by using *Saccharomyces cerevisiae*: Examination of barley as a feedstock for bioethanol production and value-added products", *Applied and Environmental Microbiology*, **75**, 1363 (2009).

Kheshgi, H. S. and R. C. Prince, "Sequestration of fermentation CO_2 from ethanol production," *Energy*, **30**, 1865 (2005).

Ko, J., W. J. Su, I. L. Chien, D. M. Chang, S. H. Chou, and R. Y. Zhan, "Dynamic modeling and analyses of simultaneous saccharification and fermentation process to produce bio-ethanol from rice straw," *Bioprocess and Biosystems Engineering*, **22**, 195 (2010).

Kwiatkowski, J. R., A. J. McAloon, F. Taylor, and D. B. Johnston, "Modeling the process and costs of fuel ethanol production by the corn dry-grind process," *Industrial Crops and Products*, **23**, 288 (2006).

Lin, Y.H., W. Chien, and K. Duan, "Correlation between reduction-oxidation potential profiles and growth patterns of *Saccharomyces cerevisiae* during very-high-gravity fermentation," *Process Biochemistry*, **45**, 765 (2010).

McCoy, S.T. "The economics of CO_2 transport by pipeline and storage in saline aquifers and oil resevoirs," Ph.D. Thesis, Department of Engineering and Public Policy, Carnegie Mellon University, Pittsburgh, PA, USA (2008).

Möllersten, K., J. Yan, and J. R. Moreira, "Potential market niches for biomass energy with CO_2 capture and storage-opportunities for energy supply with negative CO_2 emissions," *Biomass and Bioenergy*, **25**, 273 (2003).

Nevoigt, E., "Progress in metabolic engineering of *Saccharomyces cerevisiae*," *Microbiology and Molecular Biology Reviews*, **72**, 379 (2008).

Nghiem, N.P., K.B. Hicks, D.B. Johnston, G. Senske, M. Kurantz, M. Li, J. Shetty and G Konieczny-Janda, "Production of ethanol from winter barley by the EDGE (enhanced dry grind enzymatic) process," *Biotechnology for Biofuels*, **3**, 8 (2010).

Ochoa, S., A. Yoo, J. U. Repke, G. Wozny, and D. R. Yang, "Modeling and parameter identification of the simultaneous saccharification-fermentation process for ethanol production," *Biotechnology Progress*, **23**, 1454 (2007).

Pratt, P.L., J.H. Bryce, and G.G. Stewart, "The effects of osmotic pressure and ethanol on yeast viability and morphology," *Journal of the Institute of Brewing*, **109**, 218 (2003).

Rajagopalan,S., E. Ponnampalam, D. McCalla, and M. Stowers, "Enhancing profitability of dry mill ethanol plants," *Applied Biochemistry and Biotechnology*, **120**, 37 (2005).

Ramirez, E. C., D. B. Johnson, A. J. McAloon, and V. Singh, "Enzymatic corn wet milling: Engineering process and cost model," *Biotechnology for Biofuels*, **2**, 2 (2009).

Sainz, J., F. Pizarro, J. R. Pérez-Correa, and E. Agosin, "Modeling of yeast metabolism and process dynamics in batch fermentation," *Biotechnology and Bioengineering*, **81**, 818 (2003).

Taylor, F., M. J. Kurantz, N. Goldberg, A. J. McAloon, and J.C. Craig.Jr., "Dry-Grind Process for Fuel Ethanol by Continuous Fermentation and Stripping," *Biotechnology Progress*,**16**, 541 (2000).

Thambimuthu, K., 2010, "IEA Weyburn CO_2 Monitoring and Storage Project," IEA Greenhouse Gas R&D Programme. http://www.iea.org/work/2004/zets/conference/presentations/thambimuthu.pdf (2004).

Thomas, K. C. and W. M. Ingledew, "Fuel alcohol production: Effects of free amino nitrogen on fermentation of very-high-gravity wheat mashes," *Applied and Environmental Microbiology*,

56, 2046 (1990).

Thomas, K.C., S.H. Hynes, A.M. Jones, and W.M. Ingledew, "Production of fuel alcohol from wheat by VHG technology: effect of sugar concentration and fermentation temperature," *Applied Biochemistry and Biotechnology*, **43**, 211 (1993).

Wingren, A., M. Galbe, and G. Zacchi, "Techno-economic evaluation of producing ethanol from softwood: comparison of SSF and SHF and identification of bottlenecks," *Biotechnology Progress*, **19**, 1109 (2003).

Yang, D.M. "Gene expression profiling in *Saccharomyces cerevisiae* grown at different specific gravity environments," M.Sc. Thesis, Department of Chemical Engineering, University of Saskatchewan, Saskatoon, SK, Canada (2007).

Zhang, C., W. Han, X. Jing, G. Pu, and C. Wang, "Life cycle economic analysis of fuel ethanol derived from cassava in southwest China," *Renewable and Sustainable Energy Reviews*, **7**(4), 353 (2003).

Zhao, Y., and Y.H. Lin, "Growth of *Saccharomyces cerevisiae* in a chemostat under high glucose conditions," *Biotechnology Letters*, **25**, 1151 (2003).

APPENDICES

Appendix A – Experimental data used for process simulation

Table A Experimental data used for process simulation. In the first column of scenarios, different glucose concentrations in feed stream are denoted as: A = 300±6.42 g/L, B = 250±3.95 g/L, C = 200±4.99 g/L. Different redox potential control levels are denoted as: a = no control, b = -150 mV, c = -100 mV. 1 and 2 stand for different repeats of an individual scenario.

Conditions	Fermentation temperature (℃)	Aeration rate (VVM)	Fermentation time (hours)	Initial glucose concentration (g/L)	Final glucose concentration (g/L)	Final ethanol concentration (g/L)
Aa1	30	0	48	302.15	15.37	125.950
Aa2	30	0	48	294.69	20.57	125.940
Ab1	30	0.0023741	48	313.05	20.35	134.305
Ab2	30	0.0023741	48	299.31	4.71	140.384
Ac1	30	0.0076624	48	300.66	23.26	116.347
Ac2	30	0.0076624	48	303.62	2.08	121.639
Ba1	30	0	42	256.44	0	130.390
Ba2	30	0	42	246.84	0	119.614
Bb1	30	0.0003083	36	254.11	0	122.855
Bb2	30	0.0003083	36	251.52	0	121.595
Bc1	30	0.0020317	36	256.89	0	126.140
Bc2	30	0.0020317	36	254.97	0	127.715
Ca1	30	0	24	200.93	0	93.740
Ca2	30	0	24	202.18	0	94.025
Cb1	30	0.0003912	24	199.08	0	95.640
Cb2	30	0.0003912	24	202.93	0	94.040
Cc1	30	0.0254238	24	212.49	0	96.085
Cc2	30	0.0254238	24	205.71	0	96.785

Appendix B – PFD of Aspen Plus process model (Four parts to display the entire PFD)

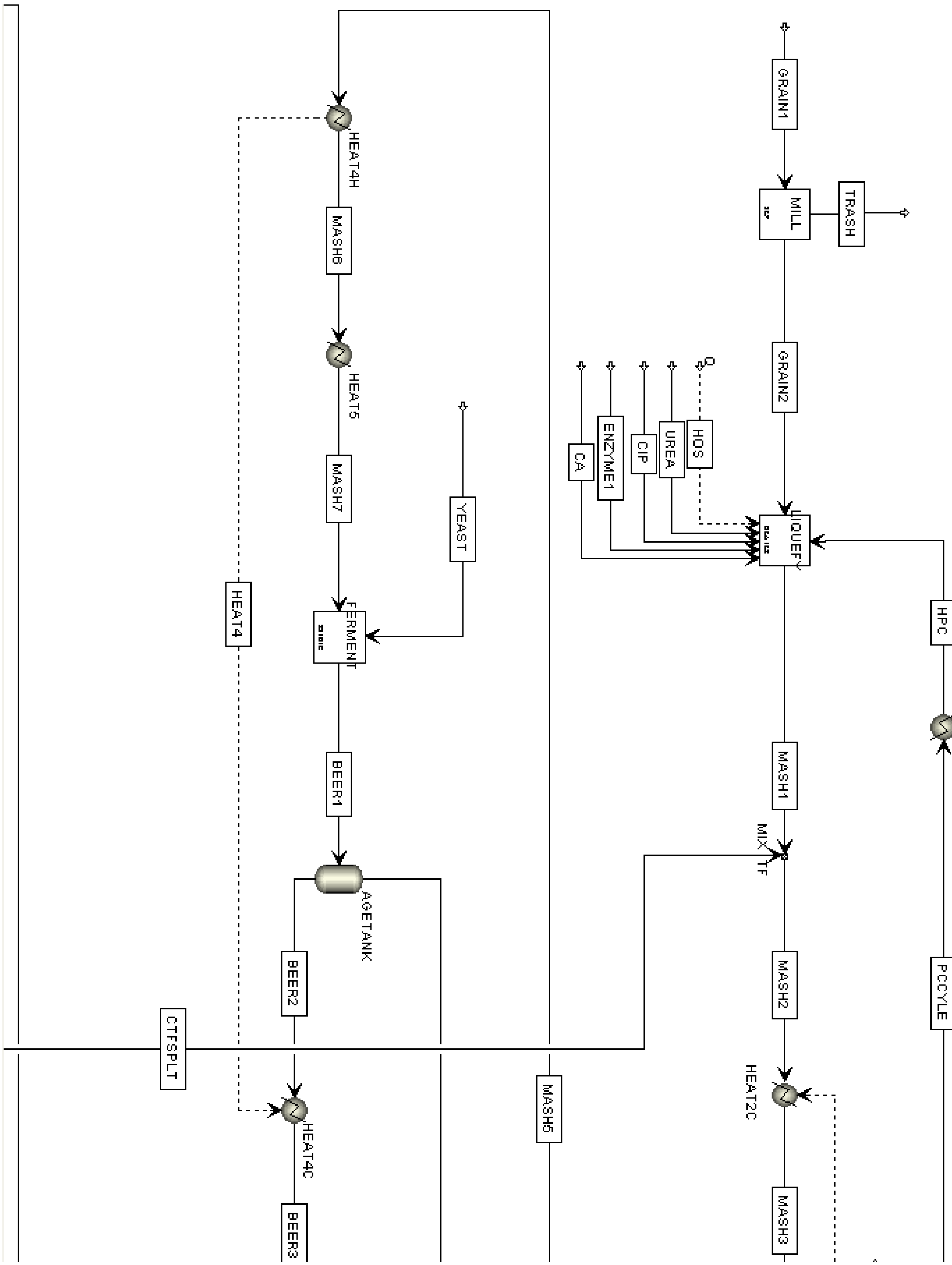

Figure B-1 PFD of Aspen Plus model (a).

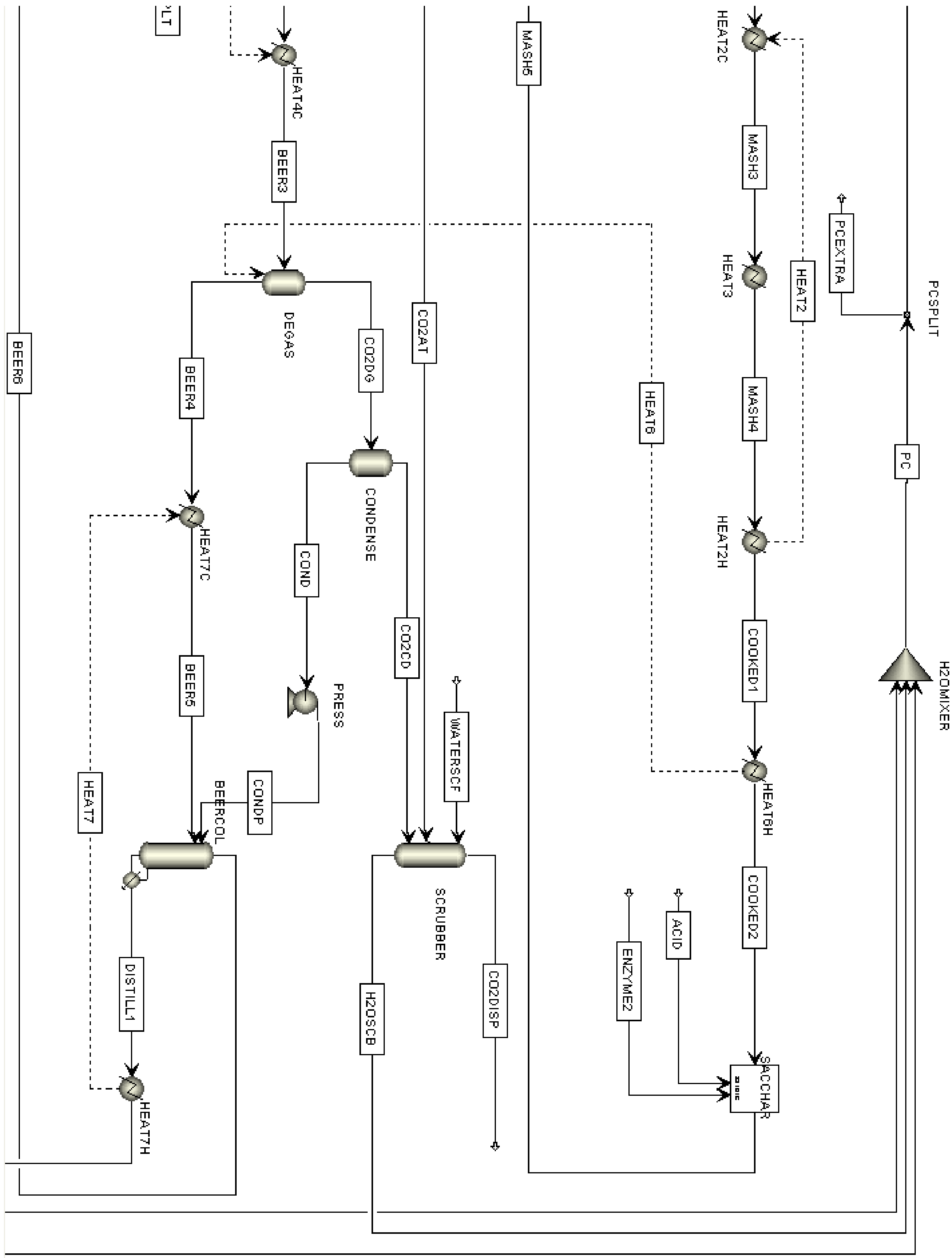

Figure B-2 PFD of Aspen Plus model (b).

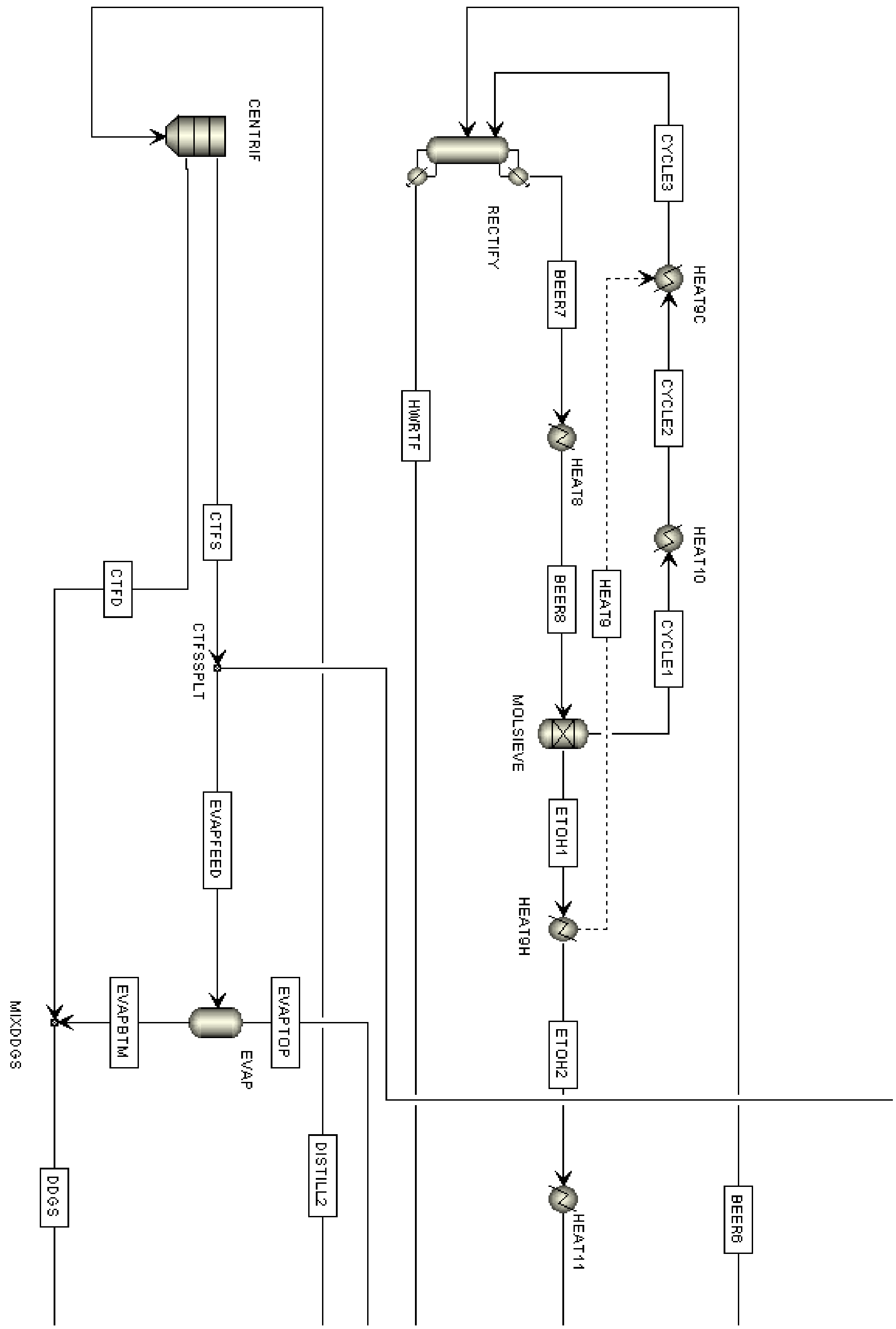

Figure B-3 PFD of Aspen Plus model (c).

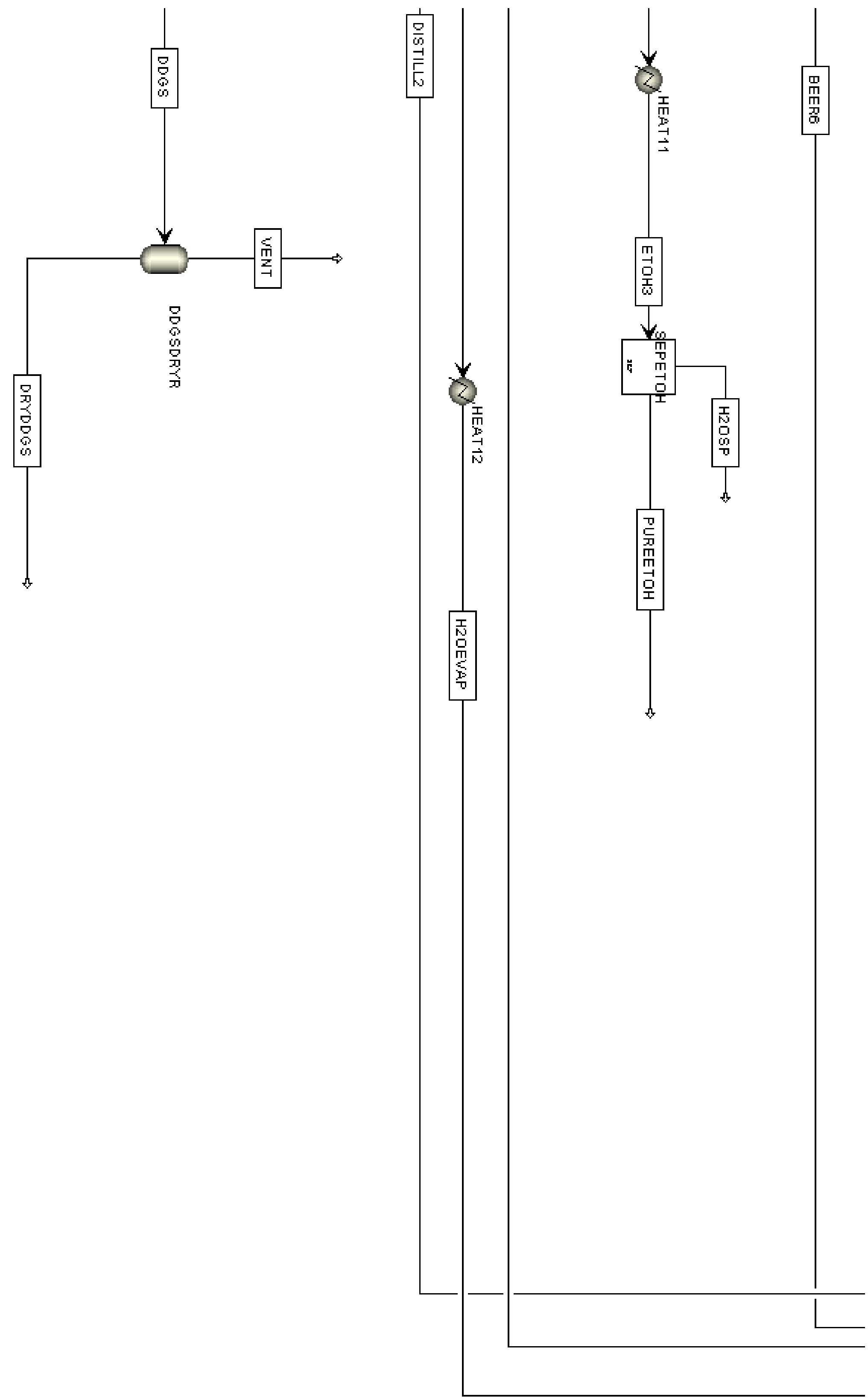

Figure B-4 PFD of Aspen Plus model (d).

Appendix C – Block definitions in Aspen Plus model

Table C-1 Reactor settings.

Block name	Block type	Temperature (F)	Pressure (psi)	Reactions	Descriptions
SACCHAR	Rstoic	140	40	Starch + Water → Glucose	Fixed fractional conversion of Starch to 0.99
FERMENT	Rstoic	90	16	Glucose → α Ethanol + α CO_2 + β YDM	Calculated fractional conversion of Glucose
				YDM → 1.13635848 Protein	Fixed fractional conversion of YDM to 0.6

Table C-2 Column settings. In stream specifications, the first capital word is the stream name used in the model, followed by its settings.

Block name	BEERCOL (Beer column)	RECTIFY (Rectifier)	SCRUBBER (CO_2 Scrubber)
Block type	RadFrac	RadFrac	RadFrac
Setup options			
Calculation type	Equilibrium	Equilibrium	Equilibrium
Number of stages	12	18	3
Condenser	None	Partial-Vapor	None
Reboiler	Kettle	Kettle	None
Valid phases	Vapor-Liquid	Vapor-Liquid	Vapor-Liquid
Convergence	Standard	Custom	Standard
Operating specifications			
Boilup ratio	Mass; 0.227	Mole; 0.228	
Reflux ratio		Mole; 2.3	
Streams			
Feed streams	CONDP; Above-Stage on Stage 1	BEER6, On-stage on Stage 10	CO2CD, On-stage on Stage 3
	BEER5, Above-Stage on Stage 1	CYCLE3, On-stage on Stage 7	CO2AT, On-stage on Stage 3
			WATERSCF, Above-Stage on Stage 1
Product streams	BEER6, leave from stage 1 in vapor phase	BEER7, leave from stage 1 in vapor phase	CO2DISP, leave from stage 1 in vapor phase
	DISTILL1, leave from stage 12 in Liquid phase	HWRTF, leave from stage 18 in liquid phase	H2OSCB, leave from stage 3 in liquid phase
Pressure profile (psi)	Stage 1: 23 psi; Stage 12: 24.5 psi	Stage 1: 20 psi; Stage 18: 24 psi	Stage 1: 15 psi

Condenser			
Subcooling specification		Subcooled temperature at 175 F, only reflux is subcooled	
Design specs	0.0005 mass purity of component Ethanol in product stream DISTILL1	0.9085 mass purity of component Ethanol in vapor of Stage 1 as internal stream	
		0.0005 mass purity of component Ethanol in total liquid of Stage 18 as internal stream	
Vary	Boilup ratio from 0.15 to 1	Reflux ratio from 1 to 5	
		Boilup ratio from 0.01 to 1	
Tray sizing			
Starting stage	1	2	
Ending stage	11	10	
Tray type	Sieve	Sieve	
Number of passes	1	1	
Tray spacing (m)	0.6096	0.6096	
Fractional approach to flooding	0.6175	0.6175	
Starting stage		11	
Ending stage		17	
Tray type		Sieve	
Number of passes		1	
Tray spacing (m)		0.6096	
Fractional approach to flooding		0.5	
Flooding calculation method		Fair	
Pack sizing			
Starting stage			1
Ending stage			3
Type			SUPER-INTX
Vendor			NORTON
Material			CERAMIC
Dimension			1-IN OR 25-MM
Height equivalent to a theoretical plate (ft)			5

Table C-3 Flash settings.

Block name	Block type	Temperature (F)	Pressure (psi)	Maximum iterations	Error tolerance
AGETANK	Flash2	90	16	30	1E -06
CONDENSE	Flash2	100	16	30	1E -06
DDGSDRYR	Flash2	220	14.7	30	1E -05
DEGAS	Flash2	184		30	1E -04
EVAP	Flash2	202.8	Vapor fraction: 0.88588	30	1E -06

Table C-4 Heater settings.

Block name	Block type	Temperature (F)	Pressure (psi)	Maximum iterations	Error tolerance
HEAT1	Heater	110	50	30	1E -05
HEAT2C	Heater		50	30	1E -05
HEAT2H	Heater	208	50	30	1E -05
HEAT3	Heater	230	50	30	1E -05
HEAT4C	Heater		30	30	1E -04
HEAT4H	Heater	112	40	30	1E -06
HEAT5	Heater	90	40	30	1E -06
HEAT6H	Heater	140	50	30	1E -05
HEAT7C	Heater		50	30	1E -04
HEAT7H	Heater	200	40	30	1E -05
HEAT8	Heater	240	19.75	30	1E -05
HEAT9C	Heater		22.5	30	1E -06
HEAT9H	Heater	184.17	14.8	30	1E -04
HEAT10	Heater	95	22	30	1E -04
HEAT11	Heater	68	18.5	30	1E -05
HEAT12	Heater	131.5	15	30	1E -05
LIQUEFY	Heater		50	30	1E -04

Table C-5 Separator settings.

Block name	MILL	MOLSIEVE	SEPETOH
Block type	Sep	Sep	Sep
Outlet stream	TRASH	CYCLE1	PUREETOH
Component split fraction			
MIXED			
Water	0.003	0.967832	0
Ethanol	0.003	0.162168	1
CO2	0.003	0.2857	0
Glucose	0.003		0
Starch			0
Protein	0.003		
Oil	0.003		
YDM	0.003		
Cpoly			0
CISOLID			
Starch	0.003		0
Protein	0.003		
Oil	0.003		
Cpoly	0.003		0
Outlet Flash			
Flash stream	GRAIN2	ETOH1	
Temperature (F)	80	240	
Pressure (psi)	14.7	18.75	
Maximum iterations	30	30	
Error tolerance	1E -04	1E -05	

Table C-6 Splitter, mixer and pump settings.

Block name	Block type	Specifications	Flash options
CENTRIF	SSplit	Stream CTFS splits 0.79746 of substream MIXED, and 0.08 of CISOLID	Maximum iterations: 30; Error tolerance: 1E -06
CTFSSPLT	FSplit	Mass flow of stream CTFSPLT = 22084.81 kg/h	Maximum iterations: 30; Error tolerance: 1E -04
H2OMIXER	Mixer		Pressure: 30 psi; Maximum iterations: 30; Error tolerance: 1E -05
MIXCTF	Mixer		Maximum iterations: 30; Error tolerance: 1E -04
MIXDDGS	Mixer		Pressure: 15 psi; Maximum iterations: 30; Error tolerance: 1E -04
PCSPLIT	FSplit	Mass flow of stream PCCYLE = 64000 kg/h	Maximum iterations: 30; Error tolerance: 1E -04
PRESS	Pump	Model: pump; Discharge pressure: 25 psi	Valid phase: Liquid-Only; Maximum iterations: 30; Error tolerance: 1E -04

Appendix D – Glossary

Abstract

Capacity: Capacity of plant for major product

Payout period: Payout Period is the expected number of years required to recover the original investment in the project. This parameter indicates the length of time that the facility needs to operate in order to recover the initial capital investment (total capital cost plus working capital).

Redox potential: Redox (shorthand for reduction–oxidation) potential (a.k.a. oxidoreduction potential, ORP) quantifies the momentary status of a biological activity, either oxidized or reduced. During fermentation, the major contributors to the changes of redox potential are NADH (served as electron donor) due to assimilatory processes such as biomass formation and dissimilatory processes such as glycolysis, and dissolved oxygen (served as electron acceptor) resulting from agitation and/or sparging. The changes of redox potential are thus related to the extent of intracellular activities to the amount of extracellular dissolved oxygen level.

Unit production cost: Is the cost associated with production divided by the number of units produced. Unit costs include all fixed costs (i.e. plant and equipment) and all variable costs (labor, materials, etc.) involved in production.

Very high gravity fermentation: Or short for VHG fermentation, fermentation with initial glucose concentration greater than 250 g/L.

Chapter 1

Liquefaction: Also known as starch liquefaction. The production of beverage alcohol from floury raw materials requires in the first place the digestion of starch by thermal pretreatment and subsequent starch liquefaction, involving the partial hydrolysis of the starch, with concomitant loss in viscosity.

Saccharification: The process of converting complex carbohydrate (e.g. starch) into simple monosaccharide components (e.g. glucose) through hydrolysis. In the production of potable distilled alcohol, the digested, liquefied starch is enzymatically split into fermentable sugar.

Saccharomyces cerevisiae: Is a species of yeast that is widely used in brewing beer. It is perhaps the most useful yeast, having been instrumental to baking and brewing since ancient times. Also called as brewer’s yeast, baker’s yeast, budding yeast or top-fermenting yeast.

Unit procedure: A unit procedure is defined as a series of operations that take place within a piece of equipment. The types of operations available depend on the type of unit procedure you are using.

Chapter 2

Ambient temperature: Ambient temperature is a term which refers to the temperature in a room, or the temperature which surrounds an object under discussion.

Azeotrope: An azeotrope is a mixture of two or more liquids in such a ratio that its composition cannot be changed by simple distillation. This occurs because, when an azeotrope is boiled, the resulting vapor has the same ratio of constituents as the original mixture. Because their composition is unchanged by distillation, azeotropes are also called (especially in older texts) constant boiling mixtures.

Azeotropic distillation: In chemistry, azeotropic distillation is any of a range of techniques used to break an azeotrope in distillation. In chemical engineering, azeotropic distillation usually refers to the specific technique of adding another component to generate a new, lower-boiling azeotrope that is heterogeneous (e.g. producing two, immiscible liquid phases).

Bio-ethanol: Biologically produced ethanol, produced by the action of microorganisms and enzymes through the fermentation of sugars or starches (easiest), or cellulose (more difficult).

Latent heat of vaporization: The heat absorbed when a substance changes phase from liquid to gas.

Molecular sieve: A molecular sieve is a material containing tiny pores of a precise and uniform size that is used as an adsorbent for gases and liquids. Molecules small enough to pass through the pores are adsorbed while larger molecules are not. Molecular sieves are often utilized in the petroleum industry, especially for the purification of gas streams and in the chemistry laboratory for separating compounds and drying reaction starting materials.

Super heater: A superheater is a device used to convert saturated steam or wet steam into dry steam used for power generation or processes. There are three types of superheaters namely: radiant, convection, and separately fired. A superheater can vary in size from a few tens of feet to several hundred feet.

Unslaked lime: Calcium oxide (CaO), commonly known as quicklime or burnt lime, is a widely used chemical compound. It is a white, caustic, alkaline crystalline solid at room temperature.

Chapter 3

Annual operating cost: The total of raw material, operating labor, maintenance, operating charges, plant overhead and G and A expenses per year.

Annual production rate: the production rate (usually the main product) on a year base.

Conversion factor: factor for adequate liquid distribution & irrigation across the scrubber bed.

Countercurrent: refer to countercurrent exchange, is a mechanism occurring in nature and mimicked in industry and engineering, in which there is an almost total crossover of some property between two flowing bodies. The flowing bodies can be liquids, gases, plasma, or even solid powders, or any combination of those.

Critical surface tension: The critical surface tension of a solid surface is an indication of its relative water-hating or water-loving character. A low critical surface tension means that the surface has a low energy per unit area. The quantity is based on experiments with a series of pure liquids.

Diffusivity: Diffusivity or diffusion coefficient is a proportionality constant between the molar flux due to molecular diffusion and the gradient in the concentration of the species (or the driving force for diffusion).

Facility type: Defines the facility type. The following types are currently available: Chemical Processing Facility, Food Processing Facility, Oil Refining Facility, Petrochemical Processing Facility, Pharmaceutical Facility, Pulp and/or Paper Processing Facility, Specialty Chemical Processing Facility (A specialty chemical is defined as a chemical which is produced in low quantity and has a usually high price per unit.). The type of facility affects the number of operators/shift and maintenance costs of facility equipment.

G and A Expenses: represents general and administrative costs incurred during production such as administrative salaries/expenses, R&D, product distribution and sales costs. Specify this number as a percentage of subtotal operating costs.

Heat transfer coefficient: The heat transfer coefficient, in thermodynamics and in mechanical and chemical engineering, is used in calculating the heat transfer, typically by convection or phase change between a fluid and a solid. Heat transfer coefficient is the proportionality coefficient between the heat flux that is a heat flow per unit area, q/A, and the thermodynamic driving force for the flow of heat (i.e., the temperature difference, ΔT).

HPLC: High-performance liquid chromatography (sometimes referred to as high-pressure liquid chromatography), HPLC, is a chromatographic technique that can separate a mixture of compounds and is used in biochemistry and analytical chemistry to identify, quantify and purify the individual components of the mixture. HPLC typically utilizes different types of stationary phases, a pump that moves the mobile phase(s) and analyte through the column, and a detector to provide a characteristic retention time for the analyte.

Installation cost: The factor is used to estimate installation cost for each piece of equipment by directly multiplying the purchase cost of the equipment.

Intermediate product: Product that has undergone a partial processing and is used as raw material in a successive productive step.

Laboratory Charges: Is a cost per period indicating the cost of having product analyzed each period.

Length of Start-up Period: After the facility has been constructed (i.e., gone through engineering, procurement and construction), the plant must go through the owner's start-up period until it starts producing the product to be sold. This period is referred to as Length of Start-up Period in weeks and is added into the EPC duration.

Material factor: The purchase cost as calculated by the options set by the purchase cost, estimates the cost of equipment assuming a reference material of construction. For all other materials, the purchase cost is adjusted by multiplying with a material-specific factor. The list of eligible materials for every equipment type and the corresponding material factors can be found in the Superpro databank.

Nominal diameter: The diameter computed for a hypothetical sphere which would have the same volume as the calculated volume for a specific sedimentary particle, also known as equivalent diameter.

NPV interest: The net present value (NPV) is a profitability measure used to evaluate the viability of an investment or to compare the profitability of a number of different investments. It represents the total value of future net cash flows during the life time of a project, discounted to reflect the time value of money at the beginning of a project (i.e., at time zero). It is calculated for three different interest rates (low, medium and high).

Operating and Maintenance Labor Escalation: is the rate at which the operating and maintenance costs of the facility are to be escalated (increased) in terms of percent per period. The operating labor costs include operators per shift and supervisory costs.

Operating Charges: Includes operating supplies and laboratory charges. It is specified as a percentage of the operating labor costs.

Operating Hours per Period: Refers to the number of hours per period that the plant will be operating.

Operating mode: Refers to the operating mode of the facility. The available options are: Continuous Processing - 24 Hours/Day, Continuous Processing - Less than 24 Hours/Day, Batch Processing - 24 Hours/Day, Batch Processing - 1 Batch per Shift, Batch Processing - More than 1 Batch per Shift, Intermittent Processing - 24 Hours/Day, Intermittent Processing - Less than 24 Hours/Day. The operating mode of the facility affects the number of operators/shift and maintenance costs of facility equipment.

Operating Supplies: Indicates the cost of miscellaneous items that are required in order to run the plant in terms of cost per period.

PID Controller: A proportional–integral–derivative controller (PID controller) is a generic control loop feedback mechanism (controller) widely used in industrial control systems – a PID is the most commonly used feedback controller. A PID controller calculates an "error" value as the difference between a measured process variable and a desired set point. The controller attempts to minimize the error by adjusting the process control inputs.

Plant Overhead: consists of charges during production for services, facilities, payroll overhead, etc. This number is specified as a percent of operating labor and maintenance costs. This number should not be used for the construction of the facility, only for operation after start-up.

Process Fluids: Indicate the types of fluids involved in the process. The selection affects operating and maintenance costs. The selections are: Liquids, Liquids and Gases, Liquids and Solids, Liquids, Gases, and Solids, Gases, Gases and Solids, Solids.

Product sales: Total product sales per period. This number is generated by multiplying Products Sales per Hour by Operating Hours per Period.

Products Escalation: Is the rate at which the sales revenue from products of the facility is to be escalated (increased) in terms of percent per period.

Project Capital Escalation: Indicates the rate at which project capital expenses may increase expressed in percent per period. If the addition of Engineer-Procure-Construct (EPC) period and start-up period is greater than one whole period, Project Capital Escalation is used to escalate the capital expenses for periods beyond the first period.

Pump efficiency: Pump efficiency is defined as the ratio of the power imparted on the fluid by the pump in relation to the power supplied to drive the pump. Its value is not fixed for a given pump, efficiency is a function of the discharge and therefore also operating head.

Raw Material Escalation: is the rate at which the raw material costs of the facility are to be escalated (increased) in terms of percent per period.

Reaction extent: The extent of reaction can be regarded as a real (or hypothetical) product, one molecule of which is produced each time the reaction event occurs. It is the extensive quantity describing the progress of a chemical reaction equal to the number of chemical transformations, as indicated by the reaction equation on a molecular scale, divided by the Avogadro constant

Revenue stream: A revenue stream is any stream that generates income. Typically, a revenue stream is an output stream that can be sold. Sometimes revenue streams are also called product streams. There may be several revenue (or product) output streams in a process.

RI detector: The refractive index (RI) detector is the only universal detector in HPLC. The detection principle involves measuring of the change in refractive index of the column effluent passing through the flow-cell. The greater the RI difference between sample and mobile phase, the larger the imbalance will become. Thus, the sensitivity will be higher for the higher difference in RI between sample and mobile phase. On the other hand, in complex mixtures, sample components may cover a wide range of refractive index values and some may closely match that of the mobile phase, becoming invisible to the detector. RI detector is a pure differential instrument, and any changes in the eluent composition require the rebalancing of the detector. This factor is severely limiting RI detector application in the analyses requiring the gradient elution, where mobile phase composition is changed during the analysis to effect the separation.

Specific surface: Specific surface area is a material property of solids which measures the total surface area per unit of mass, solid or bulk volume, or cross-sectional area. It is a derived scientific value that can be used to determine the type and properties of a material (e.g. soil). It is defined either by surface area divided by mass (with units of m^2/kg), or surface area divided by the volume (units of m^2/m^3 or m^{-1}). It has a particular importance in case of adsorption, heterogeneous catalysis, and reactions on surfaces.

Subtotal operating cost: Subtotal cost of raw materials, operating labor, utilities, maintenance, operating charges, and plant overhead.

Unit breakdown: A breakdown of the estimated unit production cost of the main product.

Utilities Escalation: User-entered percentages reflecting the anticipated utility price increase each period.

Working Capital Percentage: The working capital expressed as a percentage of total capital expense per period indicates the amount required to operate the facility until the revenue from product sales is sufficient to cover costs. It includes current assets such as cash, accounts receivable and inventories. When the facility starts producing revenue, this cost item can be covered by the product sales.

Yeast dry matter: or short for YDM, is a created component used in process models to represent biomass produced during fermentation.

Chapter 4

Greenhouse gas: sometimes abbreviated GHG, is a gas in an atmosphere that absorbs and emits radiation within the thermal infrared range. This process is the fundamental cause of the greenhouse effect. The primary greenhouse gases in the Earth's atmosphere are water vapor, carbon dioxide, methane, nitrous oxide, and ozone.

Residence time: also known as removal time, is the average amount of time that a particle spends in a particular system. This measurement varies directly with the amount of substance that is present in the system.